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Ceramic fibres from polymer precursor containing Si–O– Ti bonds

Part 1 *The formation mechanism and the pyrolysis of the polymer*

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By the reaction between organosilicon compounds and titanium alkoxides, polymers (atom ratio Ti/Si = 0.045 to 0.12) as the precursors for ceramic fibre were synthesized. Titanium in the precursors was bonded to organosilicon compounds in the Si–O–Ti bond. The synthesis process of the fibre is melt-spinning of the precursor, curing of the precursor fibre, and its heat-treatment. Curing was achieved by cross-linking of the polymer by the oxidation of Si–H bonds or hydrolysis of Ti–OR bonds in the precursor. The formation mechanism of the precursors and their pyrolysis process were examined in an inert gas atmosphere and in a vacuum. It was shown that the Si–O–Ti bond in the precursors is cleaved by pyrolysis of the Ti–O bond, so that TiC is formed. The tensile strength of the ceramic fibre obtained, is relatively high even by the heat-treatment at temperatures higher than 1200° C. Further, the Young's modulus is little changed.

1. Introduction

The method of synthesis of a ceramic fibre with an organometallic polymer as the precursor, is an excellent means of obtaining continuous fibres of diameter around 10 μm. We reported previously the method of synthesis of ceramics containing titanium with a polymer precursor [1]. We also reported the results of synthesis of a Si–Ti–C–O fibre [2]. Si–Ti–C fibre is already in industrial production [3]. These polymer precursors are synthesized by heating a mixture of the polycarbosilane synthesized by pyrolysis of poly(dimethylsilane) and the titanium alkoxide. In this reaction mechanism, it is presumed that an Si–O–Ti bond is formed by the reaction between the Si–H bond in the polycarbosilane and titanium alkoxide [1]. However, this is not shown definitely. When fibre is synthesized using a precursor with a high titanium content, its mechanical properties are low [3]. Although the reason for this is not clear, the oxide concentration in the fibre is high.

In the present study, we synthesized polymers with a high titanium content in which the organosilicon compound was bonded to titanium through the Si–O–Ti bond, expecting to obtain new materials by pyrolyzing them. Their formation mechanisms were clarified and their pyrolysis mechanisms were also examined. As an example, characteristics of the ceramic fibres (SiC–TiC fibre) synthesized with these precursors, are also reported.

2. Experimental details

2.1. Synthesis of polymers

For organosilicon compounds, the starting material were liquid polysilane (LPS) or polycarbosilane (PC), obtained by pyrolysis or pyrolitic condensation [4] of poly(dimethylsilane) under normal pressure. LPS is a low molecular weight compound formed by pyrolysis at 400° C of poly(dimethylsilane), obtained as a fraction during the pyrolysis. These polymers are represented approximately in three structural units, SiC_4, SiC_3H and SiC_xSi_{4-x}, by a method reported previously [5]. LPS and PC used in the present study are shown in Table I.

For titanium alkoxides, other starting materials, tetraisopropoxititanium (TPT), tetrabutoxititanium (TBT), or a derivative in the reaction between TPT and diphenylsilanediol in molar ratio 1 : 2 were used.

Using the above materials, and the methods of

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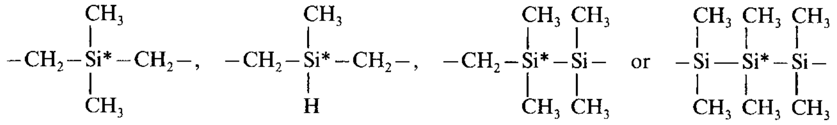
TABLE I LPS and PC; synthesis conditions, number average molecular weight, $\bar{M}_n$, and fractions of SiC_4, SiC_3H and SiC_xSi_{4-x}[†]

	Reaction temp. (°C)	Reaction time (h)	$\bar{M}_n$	SiC_4	SiC_3H	SiC_xSi_{4-x}
LPS-400	400	–	400	0	0.32	0.68
PC-400-14	400	14	1360	0.24	0.56	0.20
PC-B1.0-350[‡]	350	10	920	0.23	0.23	0.54
PC-B2.0-350[‡]	350	10	1060	0.20	0.13	0.67

[†] When PC or LPS is assumed to be in linear structure, SiC_4, SiC_3H and SiC_xSi_{4-x} correspond to the Si* atoms, respectively [5].

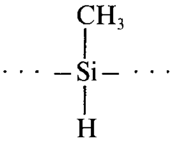


$$-CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-CH_2-,\quad -CH_2-\overset{CH_3}{\underset{H}{Si^*}}-CH_2-,\quad -CH_2-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}-\ \text{or}\ -\overset{CH_3}{\underset{CH_3}{Si}}-\overset{CH_3}{\underset{CH_3}{Si^*}}-\overset{CH_3}{\underset{CH_3}{Si}}-$$

SiC_4 SiC_3H SiC_xSi_{4-x}

[‡] As the reaction accelerator, 1 to 2 wt % borosiloxane compound is added to the poly(dimethylsilane) [4].

synthesis indicated in Fig. 1, polymers containing Ti were synthesized.



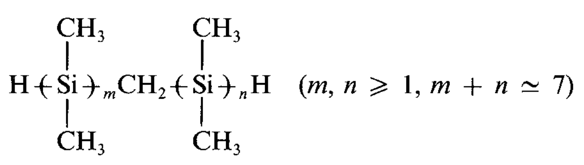
$$\cdots-\overset{CH_3}{\underset{H}{Si}}-\cdots$$

is a skeleton represented by a structural unit SiC_3H in LPS or PC as the starting material. (In fact, in the skeleton represented by SiC_xSi_{4-x}, i.e. in the polysilane skeleton, the existence of an Si–H bond is also possible. Although this will be described more fully in a future report, in the present study it is assumed that the Si–H bond exists approximately as SiC_3H.)

2.1.1. Method I

Method I, a model reaction, is intended for analysis of the reaction between PC and titanium alkoxide reported in the literature [1–3]. Therefore, LPS-400 with a low molecular weight and TPT were mixed to give the equivalent of an isopropoxy group to the Si–H bond in LPS-400. The mixture was heated in a nitrogen atmosphere at various temperatures up to 275° C, to enable the structure to be analysed.

The yield of LPS-400 obtained from poly(dimethylsilane) was 52%. From Table I, the average structure of LPS-400 is presumed to be



$$H{+}\overset{CH_3}{\underset{CH_3}{Si}}{+}_mCH_2{+}\overset{CH_3}{\underset{CH_3}{Si}}{+}_nH \quad (m, n \geq 1, m+n \simeq 7)$$

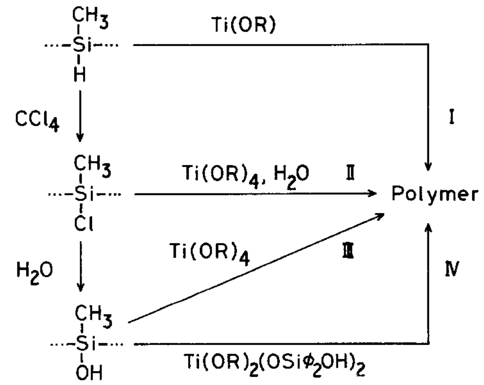


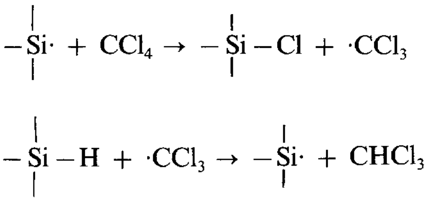
Figure 1 Methods of synthesis of organosilicon polymers containing titanium.

The polymer obtained by Reaction I is termed LPS-Ti(0.08)$_{\mathrm{I}}$ from the atomic ratio Ti/Si = 0.08 when LPS-400 and TPT were mixed.

In order to form the Si–O–Ti bond directly between LPS or PC and titanium alkoxide, $Ti(OR)_4$, the reactions described below were carried out.

2.1.2. Method II

In method II, Si–Cl as a functional group is introduced into LPS or PC, thus by cohydrolysis between Si–Cl and Ti–OR the formation of an Si–O–Ti bond is expected. The introduction of Si–Cl into LPS or PC is easily attained by refluxing it with carbon tetrachloride, CCl_4. The reaction is the same as that in which the Si–H bond in hydrosilane is converted to an Si-Cl bond with CCl_4 in the presence of an initiator for radical reaction [6]. LPS or PC in Table I already possesses a free silyl radical, so that the reaction can take place without the initiator. The mechanism is shown below.



$$-\overset{|}{\underset{|}{Si}}\cdot + CCl_4 \rightarrow -\overset{|}{\underset{|}{Si}}-Cl + \cdot CCl_3$$

$$-\overset{|}{\underset{|}{Si}}-H + \cdot CCl_3 \rightarrow -\overset{|}{\underset{|}{Si}}\cdot + CHCl_3$$

In Fig. 2, the decrease in SiC_3H and the increase in absorbance of the peak due to Si–Cl stretching vibration at 485 cm^{-1}, when PC-B2.0-350 and excess CCl_4 are refluxed at 80° C, are shown with the lapse of reaction time. These results were calculated from the measurements of the infrared absorption spectrum. SiC_3Cl is assumed to be equal to the decrement of SiC_3H. SiC_3H and its decrement can be calculated from the change in absorption intensity (Si–H stretching) at 2100 cm^{-1} in the infrared absorption spectrum [5]. The decrement in SiC_3H corresponds to the increment in absorbance of the Si–Cl bond, which thus supports the above reaction. The rate of chlorination is decreased by diluting CCl_4 with tetrahydrofuran, THF.

From PC-B2.0-350(SiC_3Cl = 0.12), the solvent was removed by distillation. THF was then added to it. Then, TBT in amounts equimolar with SiC_3Cl was

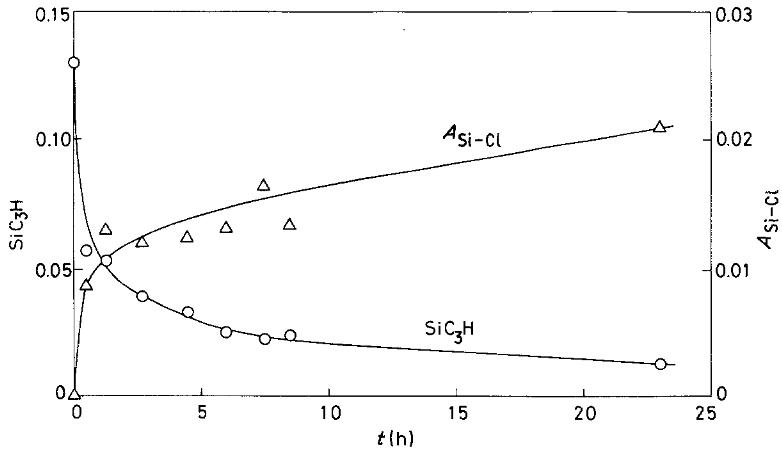
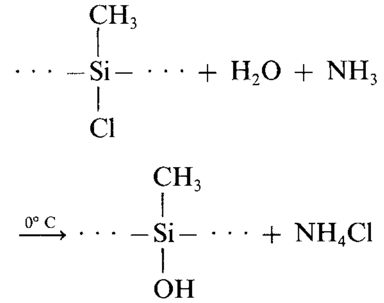


Figure 2 Change in SiC_3H and in the absorbance at $485\,cm^{-1}$, $A_{Si\text{-}Cl}$, in the infrared absorption spectrum (CCl_4 solution $20\,mg\,cm^{-3}$) during chlorination of PC-B2.0-350 with CCl_4 at 80° C.

added to the solution, and 1, 1.5 or 2 mol H_2O to 1 mol TBT was added. The mixture was refluxed overnight or longer and then concentrated by heating to 150° C. The polymer obtained is termed PC-Ti$(0.12)_{II}$ from the atomic ratio Ti/Si.

2.1.3. Method III

In method III, the silanol group is utilized, which was introduced by reacting H_2O with chlorinated LPS or PC as in Section 2.1.2. By the reaction below, Si–Cl is converted to Si–OH.



$$\cdots-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{\overset{|}{\underset{|}{Si}}}}-\cdots + H_2O + NH_3 \xrightarrow{0^\circ C} \cdots-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{Si}}}}-\cdots + NH_4Cl$$

The reaction proceeded completely by using H_2O in amounts equimolar with SiC_3Cl. In Fig. 3, for PC-B2.0-350, the decrease in the Si–Cl bond ($485\,cm^{-1}$) and the formation of an Si–OH bond (the absorption due to free O–H stretching at $3670\,cm^{-1}$) with the lapse of reaction time, followed in infrared absorption spectrum, are shown as changes in the respective absorbances. It is seen that the reaction is complete after about 1 h.

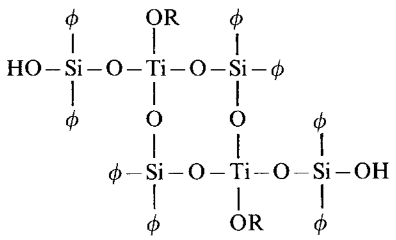
To LPS-400(SiC_3OH = 0.28) synthesized in this way, 1/4 mol TPT was added to SiC_3OH. From this mixture in THF solution, the THF was then slowly removed in a nitrogen atmosphere. It was then heated to 225° C, so that LPS-Ti$(0.07)_{III}$ was obtained.

PC-B1.0-350(SiC_3OH = 0.07) in THF solution was dropped to TPT in THF solution in amounts equimolar with SiC_3OH. It was left at room temperature overnight in a nitrogen atmosphere and continually stirred. The mixture was then heated to about 70° C to remove THF. PC-Ti$(0.07)_{III}$ was obtained.

2.1.4. Method IV

In method IV, PC in which the silanol group was introduced, is also used. However, $Ti(OR)_4$ is first reacted with diphenylsilanediol in a 1 : 2 ratio, and then reacted with PC.

When TPT and diphenylsilanediol in THF solution are reacted for 0.5 h reflux, a compound is formed with a narrow molecular weight distribution of about 1250 number average molecular weight, i.e. a dimer of $Ti(OR)_2(OSi\phi_2OH)_2$, of which the structure is presumed to be



$$\begin{array}{ccccccccc} & \phi & & OR & & \phi & & & \\ & | & & | & & | & & & \\ HO- & Si & -O- & Ti & -O- & Si & -\phi & & \\ & | & & | & & | & & & \\ & \phi & & O & & O & & \phi & \\ & & & | & & | & & | & \\ & & \phi- & Si & -O- & Ti & -O- & Si & -OH \\ & & & | & & | & & | & \\ & & & \phi & & OR & & \phi & \end{array}$$

ϕ: phenyl group

R: isopropyl group

In its infrared absorption spectrum, the absorption peak at 2980 to $2860\,cm^{-1}$ due to the C–H stretching vibration apparently indicated the existence of isopropyl groups. Then, corresponding to this, the absorption in the vicinity of $3600\,cm^{-1}$ indicated the

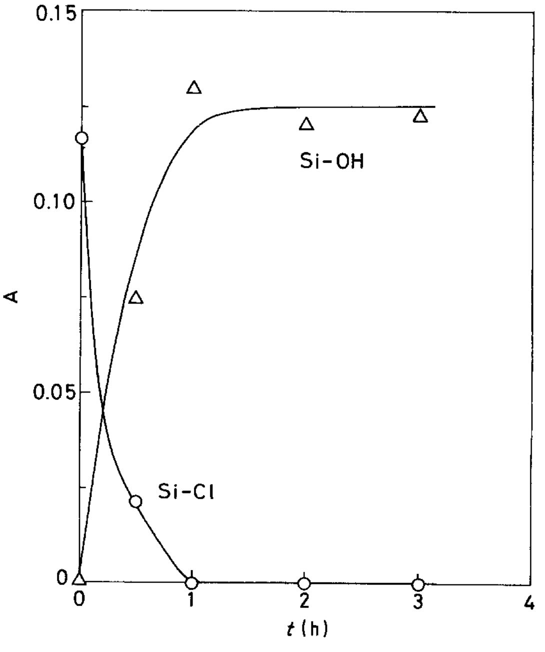


Figure 3 Change in absorbance, A, of Si–Cl ($485\,cm^{-1}$) and Si–OH ($3670\,cm^{-1}$) in the infrared absorption spectrum (CCl_4 solution $100\,mg\,cm^{-3}$) of PC-B2.0-350 during conversion of Si–Cl to Si–OH by hydrolysis.

TABLE II Melt spinning and curing conditions of the precursor fibres

Precursor	Spinning condition		Curing condition†
	T(°C)	d(μm)*	
PC-Ti(0.12)$_{\text{II}}$	130	20–26	Leaving in air for 1 day or more.
PC-Ti(0.07)$_{\text{III}}$	160	11–12	In air at 110°C for 1 h.
PC-Ti(0.045)$_{\text{IV}}$	320	18–26	In oxygen stream at 190°C for 1 h.
PC-Ti(0.083)$_{\text{IV}}$	260	14–18	In oxygen stream at 150°C for 1 h.

*Average diameter of SiC–TiC fibre.

†On heating at the rate of $10°\mathrm{C\,h^{-1}}$ from room temperature.

remaining Si–OH. Further, a strong absorption peak appeared at $920\,\mathrm{cm^{-1}}$ due to the absorption by the Si–O–Ti bond [7, 8].

The dimer of 1/4 mol SiC_3OH in THF solution was added to LPS-400(SiC_3OH = 0.30), and the dimer of 1/2 mol SiC_3OH was added to PC-400-14 (SiC_3OH = 0.05) or PC-400-14(SiC_3OH = 0.10). THF was then slowly removed from the mixture by distillation while stirring in a nitrogen atmosphere. On heating up to 250°C, LPS-Ti(0.12)$_{\text{IV}}$ was then synthesized, on heating at 300°C for 1 h, PC-Ti(0.045)$_{\text{IV}}$ was obtained, and by heating at 200°C for 1 h, PC-Ti(0.083)$_{\text{IV}}$ was obtained.

2.1.5. Other polymers

As a polymer for comparison, solid polytitanoxane was obtained by adding 29/30 mol H_2O to 1 mol TPT and refluxing the mixture in isopropyl alcohol in a nitrogen atmosphere, then removing the solvent and subsequently heating to 240°C.

Another polymer, polytitanosiloxane, was also obtained by refluxing a mixture of diphenylsilanediol and TBT in molar ratio 3 : 1 in xylene solution in a nitrogen atmosphere, then removing the solvent and heating to 300°C.

2.2. Synthesis of SiC–TiC fibres

Conditions of synthesis of the SiC–TiC fibres are shown in Table II. Of the polymers synthesized in Section 2.1, the polymers in Table II were used as precursors. The precursors were melt-spun into fibre which was then cured by leaving in atmospheric air, or heating under oxygen at a flow rate of $50\,\mathrm{cm^3\,min^{-1}}$. Subsequently, the fibre was heat treated at 1100 to 1500°C under an argon stream at a flow rate of $200\,\mathrm{cm^3\,min^{-1}}$ or in a vacuum of $< 3 \times 10^{-3}$ torr at a rate of $100°\mathrm{C\,h^{-1}}$, and held at this specific temperature for 1 h.

2.3. Measurements on polymers and fibres

The infrared absorption spectra were measured using a Hitachi 295 infrared spectrophotometer, by the CCl_4 solution method and a KBr fixed cell of thickness 0.2 mm or by the KBr disc method.

The molecular weight and molecular weight distribution were measured using a Hitachi 655 liquid chromatograph, with Shodex A-804 as the GPC column and a wavelength 254 nm supplied from a variable wavelength ultraviolet monitor. As the eluent, THF at a flow rate of $1\,\mathrm{ml\,min^{-1}}$ was used. The number average molecular weight, $\bar{M}_n$, was measured using an intelligent integrator model 7000 AS (System Instruments Co., Tokyo, Japan) using the measured value of the GPC chromatogram with polystyrene as the standard reference.

Mechanical properties of the fibres, i.e. the tensile strength and Young's modulus, were measured with a universal testing machine UTM-II-20 (Toyo Baldwin Co., Tokyo, Japan) using a gauge length of 25 mm and a cross-head speed of $2\,\mathrm{mm\,min^{-1}}$. Thirty specimens of the fibres were measured.

X-ray diffraction patterns (Cu$K\alpha$) of the fibres was measured with using a Rotaflex RU-200 (Rigaku Denki Co., Tokyo, Japan).

In examination of the pyrolytic processes of polymers and precursor fibres, for infrared absorption spectrum measurements, the KBr disc was heat-treated repeatedly at 200 to 700°C for 1 h under a nitrogen stream at a flow rate of $100\,\mathrm{cm^3\,min^{-1}}$ [9].

3. Results and discussion

3.1. Structures of the polymers

Methods I to IV in Fig. 1 are intended for synthesis of the organosilicon polymers containing titanium. In the reaction between PC and $Ti(OR)_4$, it is presumed conventionally that $-Ti(OR)_3$ becomes a pendant group to PC through the Si–O–Ti bond, or otherwise PC is cross-linked by, for example, $-Ti(OR)_2-$ [1]. However, the existence of Si–O–Ti is not confirmed yet. When the Si–O–Ti bond is formed, a strong absorption in the infrared absorption spectrum is observed in the vicinity of $920\,\mathrm{cm^{-1}}$, as in the case of $Ti(OR)_2(OSi\phi_2OH)_2$. Because the dimer $Ti(OR)_2(OSi\phi_2OH)_2$ is formed in a short time, it is presumed that the reaction in method III proceeds easily. Therefore, LPS-Ti(0.07)$_{\text{III}}$ in method III is considered to be a model reaction for forming the Si–O–Ti bond by the reaction between LPS or PC and $Ti(OR)_4$.

In Fig. 4 the reaction between LPS-400(SiC_3OH = 0.28) and TPT, followed by infrared absorption spectrum, is shown. Immediately after LPS-400 and TPT in THF are mixed together, strong absorption appears at $900\,\mathrm{cm^{-1}}$. However, with lapse of time the peak is reduced. In THF, even on heating at 70°C, the intensity is not increased. Although the reason is not clear, when THF is removed slowly by distillation at 70°C, a peak at $900\,\mathrm{cm^{-1}}$ appears which is stronger than immediately after the mixing.

In Fig. 5, change in absorbance of the peak at $900\,\mathrm{cm^{-1}}$ with temperature is shown; the reaction time at each temperature is 1 h. The Si–O–Ti bonds increase gradually up to 175°C. Beyond this point, they decrease, indicating decomposition of the Si–O–Ti bonds.

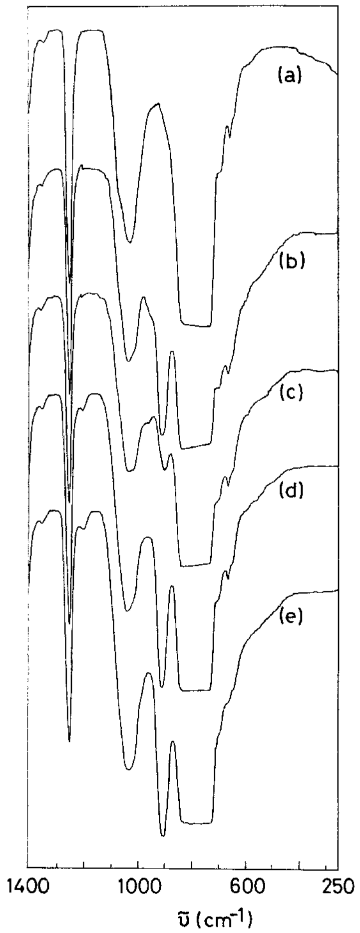


Figure 4 The reaction between LPS-400(SiC_3OH = 0.28) and TPT followed by infrared absorption spectrum: (a) LPS-400 (SiC_3OH = 0.28); (b) after 10 min at room temperature; (c) for 1 h at 70° C in THF; (d) for 1 h at 70° C after removing THF; (e) for 1 h at 200° C.

The molecular weight distribution of LPS-400 and LPS-Ti$(0.07)_{III}$ obtained at 70° C after removal of THF is shown in Fig. 6. Molecular weight distribution of LPS-400 is little changed by chlorination and hydrolysis. In LPS-Ti$(0.07)_{III}$, up to the point when THF is removed, a rise in its molecular weight is hardly seen. After removal of THF, its molecular weight is increased, as shown in Fig. 6. In Fig. 5, the fraction of unreacted LPS and/or LPS with a molecular weight of about 400, reproduced by the decomposition of LPS-Ti$(0.07)_{III}$, f_{LPS}, is shown. f_{LPS} was calculated by integration of the GPC curve. The result shows that the reaction is nearly complete at 70° C. The reason for unreacted LPS seems to be that chlorination of LPS is insufficient, so that about 13% SiC_3H remains. The increase in f_{LPS} beyond 175° C thus indicates the decomposition of the Si–O–Ti bond. In fact, at reaction temperatures beyond 175° C a crystalline solid begins to separate. From GPC and the infrared absorption spectrum, this was found to be a substance of number average molecular weight 360, containing cyclic siloxane bonds. Also in Fig. 4, the reaction at high temperature increases the absorption peak at 1030 cm⁻¹, showing the formation of an Si–O–Si bond.

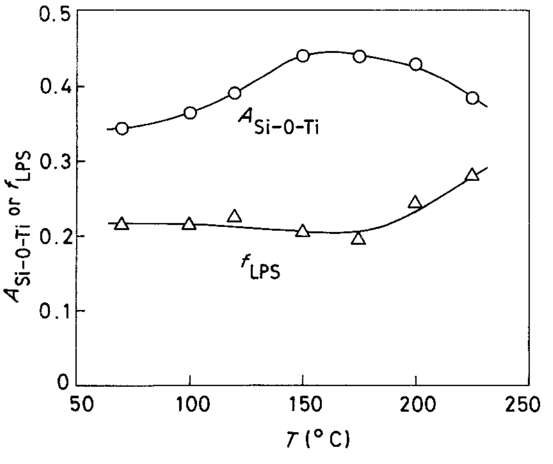


Figure 5 Change in the absorbance, $A_{Si-O-Ti}$, at 900 cm⁻¹ in the infrared absorption spectrum (CCl_4 solution 20 mg cm⁻³) and in the fraction of unreacted LPS, f_{LPS}, by GPC in LPS-Ti$(0.07)_{III}$.

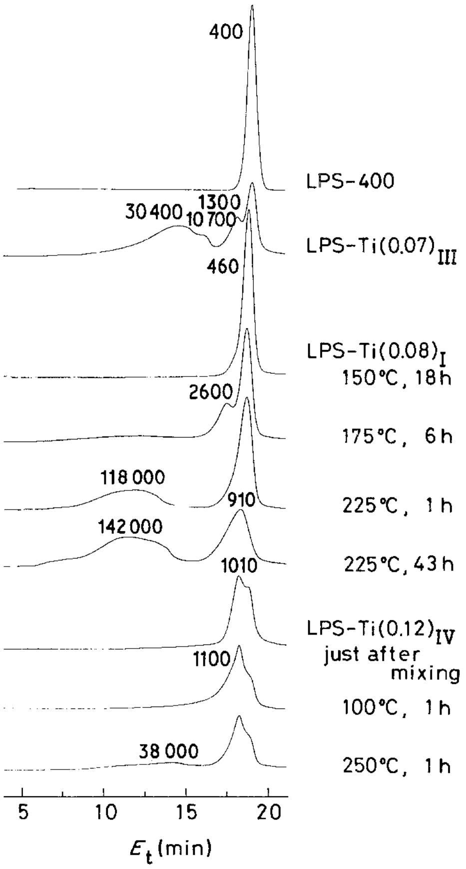
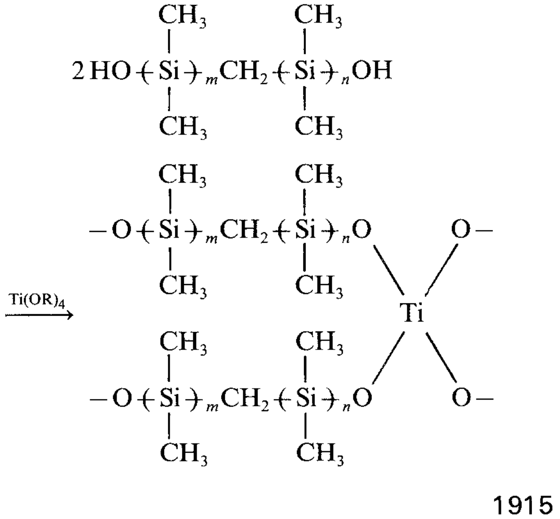


Figure 6 GPC curves of LPS-400, LPS-Ti$(0.07)_{III}$ obtained at 70° C, LPS-Ti$(0.08)_I$ and LPS-Ti$(0.12)_{IV}$ (numbers in the figure are peak molecular weights).

From the above results, the formation mechanism of LPS-Ti$(0.07)_{III}$ is presumed to be as follows; the structure is composed of networks of cross-linked LPS with Ti



$$2\,\mathrm{HO}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!m}\mathrm{CH_2}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!n}\mathrm{OH}$$

$$\xrightarrow{\mathrm{Ti(OR)_4}}\quad \begin{array}{l}-\mathrm{O}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!m}\mathrm{CH_2}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!n}\mathrm{O}\qquad\quad \mathrm{O}-\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown\quad\diagup\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{Ti}\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \diagup\quad\diagdown\\ -\mathrm{O}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!m}\mathrm{CH_2}\!\left(\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!n}\mathrm{O}\qquad\quad \mathrm{O}-\end{array}$$

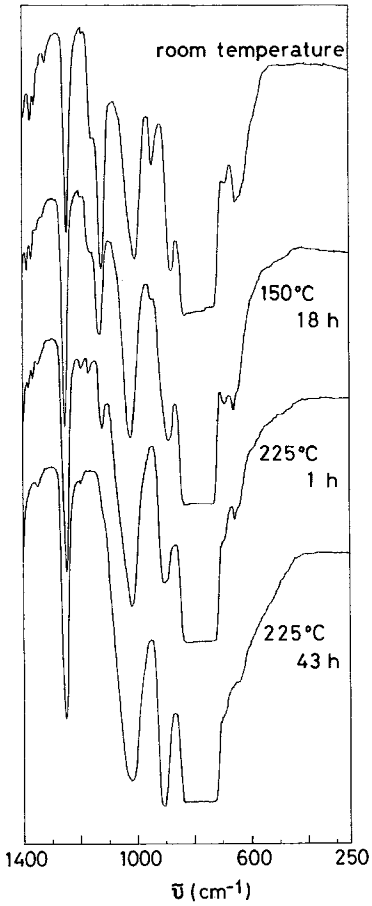


Figure 7 Infrared absorption spectra of LPS-Ti(0.08)$_I$ obtained in the reaction between LPS-400 and TPT.

The structure of LPS-Ti(0.08)$_I$ was also examined from the infrared absorption spectrum and by GPC. In Fig. 7, the reaction as followed by the infrared absorption spectrum, is shown. It is seen that LPS-400 reacts with TPT and an absorption peak at 900 cm^{-1} appears due to the Si–O–Ti bond. In Fig. 6, the change in its molecular weight distribution determined by GPC is shown. As seen, there is a correlation between the formation of the Si–O–Ti bond and the increase in its molecular weight. From examination of the correlation with the Si–H bond in LPS-400, the change in decrement of SiC_3H with the reaction temperature is as shown in Fig. 8. At high temperature the rate of decrease of SiC_3H accelerates, in agreement with the results obtained by infrared absorption spectrum or by GPC. However, as indicated in Fig. 8, the change in absorbance at 900 cm^{-1} due to the Si–O–Ti bond is not in linear relation with the decrement in SiC_3H. Further, the molecular weight changes in correspondence with the absorbance in the absorption at 900 cm^{-1}, rather than with the decrement in SiC_3H. This indicates that the absorption intensity at 900 cm^{-1} is largely dependent on the molecular structure. As indicated in Fig. 6, when reacted at 225° C for over 1 h, the remaining ratio of SiC_3H is similar to that in LPS-Ti(0.07)$_{III}$, but the molecular weight distribution is quite different. This is evidently due to the difference in the reaction mechanism.

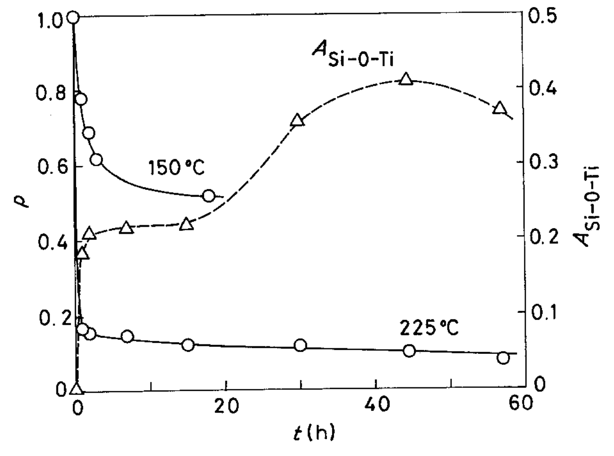
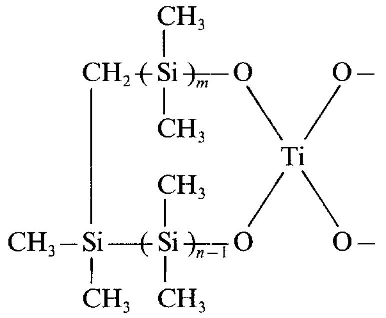


Figure 8 Change in the ratio of remaining SiC_3H (p) in the reaction between LPS-400 and TPT and absorbance, $A_{Si-O-Ti}$, at 900 cm^{-1} in the infrared absorption spectrum (CCl_4 solution 20 mg cm^{-3}) in the reaction at 225° C.

In review of the structure of the formula already mentioned from the comparison of LPS-Ti(0.08)$_I$ and LPS-Ti(0.07)$_{III}$, in method III the reaction proceeds rapidly at low temperature and the molecular weight is smaller than that in method I. It is therefore presumed that the ring formation between LPS and TPT in method III suppresses an increase in its molecular weight. The ring structure is then considered to be



The formation of this ring structure may be accelerated by the use of a solvent in the initial stage of the reaction. In method I, on the other hand, the mechanism initiating formation of the Si–O–Ti bond is not definite. However, in the peaks corresponding to components of the lowest molecular weights in the respective polymers in Fig. 6, the peak does not shift with rise in the reaction temperature in method III, but in method I the peak shifts largely to higher molecular weights. In method I, therefore, there is little cessation of growth of the polymer chain by formation of the ring. It is thus indicated that in method I control of the reaction is difficult.

The control of the reaction by method III is shown in PC-Ti(0.07)$_{III}$. Because in this reaction SiC_3OH and TPT are equimolar, by dropping PC into TPT, $-Ti(OR)_3$ should be introduced as a pendant group to PC, and not that PC is cross-linked by TPT. GPC measurements showed that the molecular weight distribution after the reaction was nearly the same as that of PC before the reaction. Infrared absorption spectra showed that isopropoxy groups remain in the polymer as expected.

Method IV is an application of method III. It was indicated in the synthesis process of the polymers in methods I and III that the Si–O–Ti bond decomposes gradually at temperatures above 200° C. In the reaction between $Ti(OR)_4$ and diphenylsilanediol in Section 2.1.5, an Si–O–Ti bond was formed and so it produced polytitanosiloxane. In this case, however, the Si–O–Ti bond is hardly decomposed, even at 300° C. Paying attention to this point, in method IV, in place of $Ti(OR)_4$, the dimer of $Ti(OR)_2(OSi\phi_2OH)_2$ is used in order to increase the heat resistance in the polymer. In the dimer there are alkoxy and hydroxy groups. The reaction with PC is thus presumed to be more complex than in method III.

Fig. 6 shows the change in molecular weight distribution detected by GPC in the reaction process of LPS-Ti$(0.12)_{IV}$. At a reaction temperature of 100° C no remarkable increase in the molecular weight was observed; only a decrease in the peak due to the unreacted LPS and the broadening in molecular weight distribution were seen. However, on increasing the reaction temperature, a broad peak appears at high molecular weights. This indicates that the reaction between SiOH in PC and alkoxy groups in the dimer takes place, and then at higher temperatures a condensation occurs between the SiOH in the dimer. Therefore, the molecular structure is a complex one, containing Si–O–Ti and Si–O–Si bonds. Stability of the Si–O–Ti bond in the polymer obtained is described later.

In method II, it was shown by infrared absorption spectroscopy that in the reaction between Si–Cl in PC and $Ti(OR)_4$, the formation of the Si–O–Ti bond by cohydrolysis is very slight. The results obtained by GPC also showed that PC is hardly cross-linked with $Ti(OR)_4$. Therefore, PC-Ti$(0.12)_{II}$ obtained is considered to be a mixture of PC and polytitanosiloxane.

3.2. Pyrolysis of the Si–O–Ti bond

In the polymers obtained by methods I, III and IV, the pyrolysis of the Si–O–Ti bond was examined by its pyrolysis in the KBr disc for infrared absorption spectrum measurement.

The results of pyrolysis of LPS-Ti$(0.07)_{III}$ are shown in Fig. 9. Other polymers also exhibited similar changes. The absorption peak at 900 cm^{-1} decreases with increasing temperature, and almost disappears at 350° C. The change in absorbance of the peak at 900 cm^{-1} is shown in Fig. 10, together with the results for other polymers. As already described, it is seen that the thermal stability of the Si–O–Ti in LPS-Ti$(0.12)_{IV}$ is especially high. The stability of the Si–O–Ti bond is an important factor for the spinnability of the molten polymer when it is melt-spun.

The stability is also linked to structure and properties of the ceramics formed by pyrolysis. Pyrolysis at lower temperatures may lead to an increase in the non-uniformity through precipitation.

In the pyrolysis mechanism of the Si–O–Ti bond, as in Fig. 9, decomposition occurs in the Ti–O bond and the absorption in the vicinity of 1020 cm^{-1} increases, so the Si–O–Si bond forms. Then, the broad peak in the vicinity of 600 cm^{-1}, presumed to be due to Ti–O bonds, which appears on heating polytitanoxane as described later, also decreases with increasing temperature. So, oxygen bonded to a titanium atom is removed as a siloxane bond, so that TiC forms at high temperature.

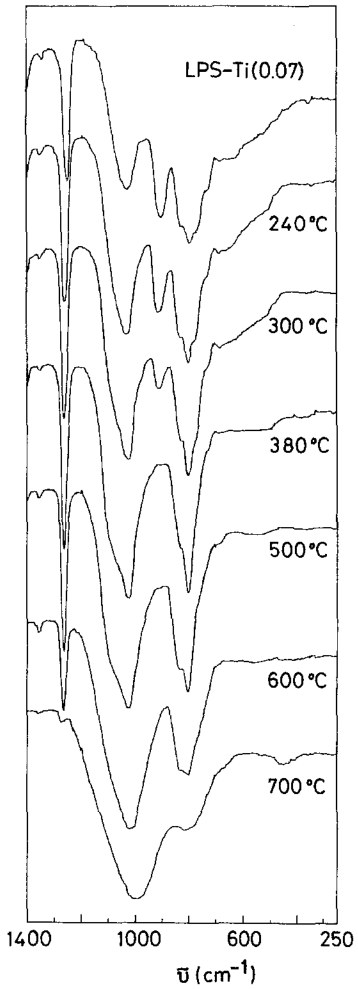


Figure 9 Change in the infrared absorption spectrum of LPS-Ti$(0.07)_{III}$ pyrolysed in the KBr disc.

Pyrolytic products at high temperature are described below.

3.3. SiC–TiC fibre

Polymers usable as precursors for SiC–TiC fibre are shown in Table II. The polymer as the precursor synthesized by method I from PC was reported previously [2, 3]. As already described, control of

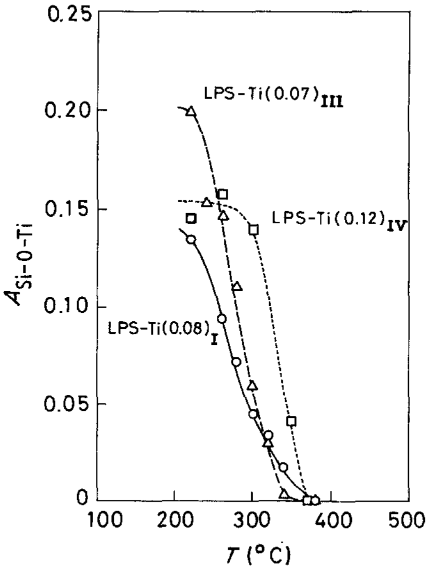


Figure 10 Change in the absorbance, $A_{Si-O-Ti}$, at 900 cm^{-1} in the infrared absorption spectrum of LPS-Ti pyrolysed in the KBr disc with pyrolytic temperature.

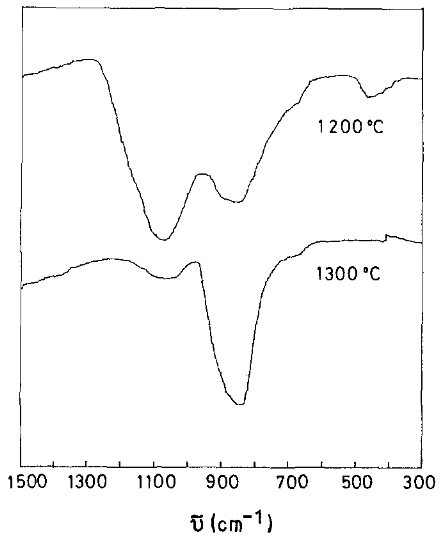


Figure 11 Infrared absorption spectra of the fibres obtained from PC-Ti(0.12)$_{II}$ by heat treatment in a vacuum.

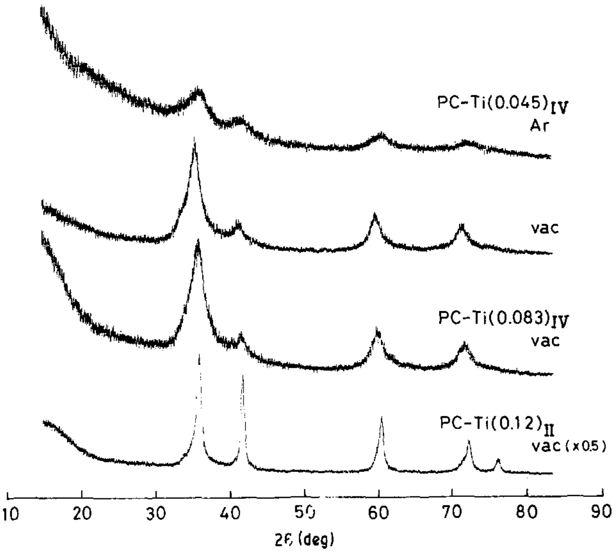


Figure 12 X-ray diffraction patterns (Cu*Kα*) of the fibres obtained from respective PC-Ti at 1300° C in a vacuum or argon atmosphere.

the reaction in method I is difficult. Therefore, the polymer obtained by method III, in which the structure could be easily controlled, was used.

In the fibre obtained from PC-Ti(0.12)$_{II}$ as the precursor, possibly due to heterogeneity of the polymer, the diameters of the fibres were not uniform, so that the mechanical properties could not be measured accurately. However, when heat-treated in a vacuum, the tensile strength and Young's modulus increased gradually up to 1200° C; the values at this temperature were about 0.7 and 130 GPa, respectively. These values then dropped rapidly at 1300° C. In the infrared absorption spectra of Fig. 11, a rapid decrease in Si–O bonds and the formation of SiC are observed. The X-ray diffraction pattern of the fibre heat-treated at 1300° C is shown in Fig. 12. The peak at $2\theta \simeq 35.7°$ corresponds to (1 1 1) of β-SiC and TiC, and the peak at $2\theta = \sim 41.7°$ mainly to (2 0 0) of TiC, so that the formation of β-SiC and TiC is indicated [2, 10, 11].

Fig. 13 shows the tensile strength and Young's modulus for the fibres obtained from PC-Ti(0.045)$_{IV}$ and PC-Ti(0.083)$_{IV}$ as precursors on heat-treating in a vacuum. In the fibres obtained from the precursors in method IV, the decrease in tensile strength at temperatures above 1200° C is slight and the Young's modulus does not decrease with increasing heat-treatment temperature.

On heat treatment under an argon atmosphere, however, in the case of PC-Ti(0.045)$_{IV}$ the tensile strength decreased, e.g. 0.77, 0.74, 0.52 and 0.04 GPa at 1200, 1300, 1400 and 1500° C, respectively, and the Young's modulus decreased similarly, e.g. 91, 92, 79 and 22 GPa, at the respective temperatures.

In Fig. 14, in the case of PC-Ti(0.045)$_{IV}$, the change in infrared absorption spectrum with the heat-treatment temperature is shown both in a vacuum and under an argon atmosphere. Under the latter atmosphere, between 1400 and 1500° C the absorption due to the Si–O bond (1100 to 1000 cm^{-1}) decreased rapidly, so that Si–C (900 ~ 800 cm^{-1}) was formed. The tensile strength and Young's modulus did not decrease up to 1300° C. However, the Young's modulus was relatively low as compared with that in a vacuum because the quantity of Si–O was large. In a vacuum, the quantity of Si–O at 1300° C was low. Corresponding with this, the Young's modulus of the

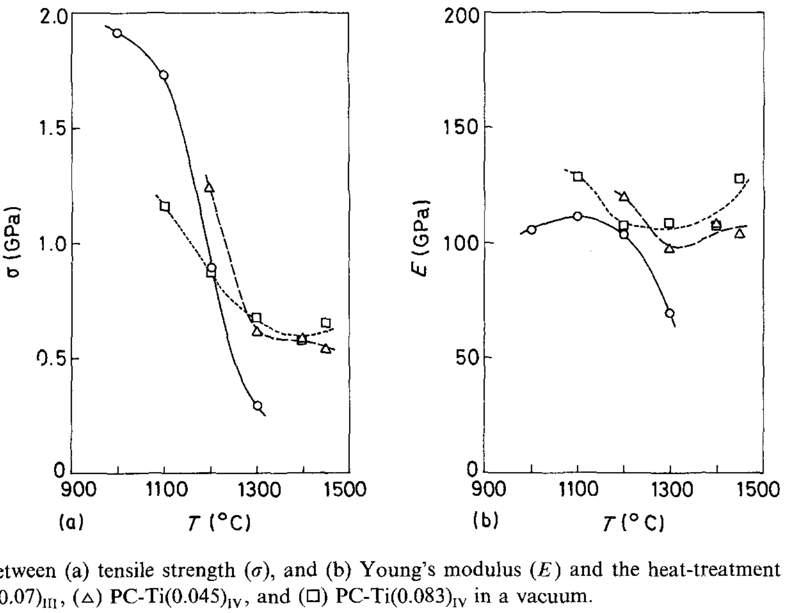


Figure 13 The relations between (a) tensile strength (σ), and (b) Young's modulus (E) and the heat-treatment temperature in the fibres obtained from (○) PC-Ti(0.07)$_{III}$, (△) PC-Ti(0.045)$_{IV}$, and (□) PC-Ti(0.083)$_{IV}$ in a vacuum.

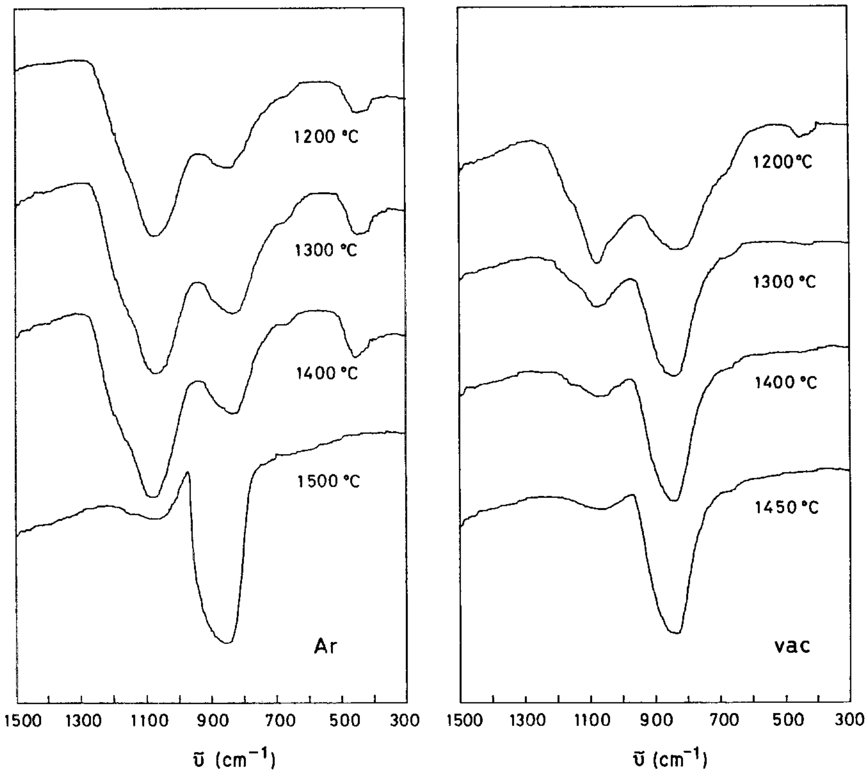


Figure 14 Change in the infrared absorption spectrum with heat-treatment temperature in the fibres obtained from PC-Ti(0.045)$_{\mathrm{IV}}$ in a vacuum and under an argon atmosphere.

fibre obtained by heat-treatment in a vacuum did not decrease at high temperature, and the tensile strength did not decrease beyond 1300° C.

Fig. 12 shows the X-ray diffraction patterns of the PC-Ti(0.045)$_{\mathrm{IV}}$ fibres heat treated at 1300° C both in a vacuum and under an argon atmosphere, and in the PC-Ti(0.083)$_{\mathrm{IV}}$ fibre heat treated at 1300° C in a vacuum. In the fibre obtained from the precursor in method IV, it is seen that the size of crystallites was small, compared with that in method II. Then on comparison of PC-Ti(0.045)$_{\mathrm{IV}}$ in a vacuum with that under an argon atmosphere, the diffraction peak due to β-SiC is intense possibly because at 1300° C a highly crystallized β-SiC is formed from the Si–O bond and free carbon. This is also supported by the results of the infrared absorption spectrum in Fig. 14.

Characteristics of the fibre obtained by heat treating the PC-Ti(0.07)$_{\mathrm{III}}$ precursor in a vacuum are shown in Fig. 13. With increasing heat-treatment temperature, both the tensile strength and Young's modulus rapidly decreased. From infrared absorption spectrum, this was seen to be due to the decrease of Si–O and the formation of Si–C. In PC-Ti(0.07)$_{\mathrm{III}}$ the alkoxy groups remain, so even in air at room temperature, curing was possible by the Ti–O–Ti bond on hydrolysis of the alkoxy group. Even by the curing conditions in Table II, the Ti–O–Ti bond forms. When Ti–O–Ti bond exists in the precursor fibre, at high temperatures the properties of the fibre may be lowered. In method II precursor, Ti–O–Ti exists in large quantities as polytitanoxane. In the Ti–O–Ti bond, i.e. in the localization of titanium, as indicated in Fig. 12, large crystallites of TiC are formed. This may lower properties of the fibre due to the phase separation in the crystallization of β-SiC and TiC.

On the other hand, in method IV precursor, possibly only the Si–O–Ti bond exists. As already described, the Si–O–Ti bond is cleaved into Ti–O. Consequently, the higher the concentration of Si–O–Ti bonds, the more easily is produced TiC possibly in a finely dispersed amorphous form.

Pyrolysis of polytitanoxane, in a vacuum at 1400° C, for example, only gave lower oxides than TiO_2, such as Ti_7O_{13}, Ti_6O_{11} and Ti_8O_{15}. Also in the infrared absorption spectrum, a single broad peak was observed in the vicinity of $600\,\mathrm{cm}^{-1}$. In contrast, in the case of polytitanosiloxane, β-SiC and TiC were formed, so that the importance of the Si–O–Ti bond for the formation of TiC is indicated.

In the precursor containing Si–O–Ti bonds, the concentration of Si–O bonds, in the fibre obtained by heat-treatment, tends to become high, so that the mechanical properties of the fibre tend to become low. In the case of the precursor without alkoxy groups the precursor fibre should be cured by cross-linking between the PC containing Si–H bonds, under the conditions shown in Table II. Oxidation of Si–H bonds forms Si–O–Si bonds, so the properties of the fibre tend to become low. To lower the concentration of Si–O in the fibre, the molecular structure should be studied.

4. Conclusions

In SiC–TiC fibre synthesized from a polymer containing titanium as the precursor, it appears that the structure and mechanical properties are dependent on the concentration of Si–O–Ti bonds. When the concentration of Si–O–Ti is high, TiC appears in a finely dispersed state. Consequently, crystal growth of β-SiC at high temperature is suppressed, so that the decrease in properties of the fibre is prevented. In this report, the synthesis of polymers containing titanium was mainly described. In the future, the method of synthesis of the polymer will be further studied and the structure of the polymer and structure and properties of the fibre will be examined in detail.

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