JOURNAL OF MATERIALS SCIENCE 26 (1991) 5167–5170

Synthesis of SiC fibre with low oxygen content and high tensile strength using a polyblend precursor

YIMING YANG, XINWEI LIU, ZILIE TAN, SHUJIN YANG, YI LU, CHUNGXIANG FENG
Changsha Institute of Technology, Changsha, People's Republic of China

SiC fibre with low oxygen content and high tensile strength was first synthesized in our laboratory. The SiC fibre was obtained by using a polyblend of polycarbosilane (PC) and hydroxy-terminated-polybutadiene (HTPB) as a precursor. It was found that PC could react with HTPB to form cross-linked polymers at temperatures around 260 °C, so the HTPB can be used as a curing agent. Consequently, the need for oxygen to be introduced in the air-curing process is reduced and SiC fibre with low oxygen content and higher tensile strength can be made. The chemical compositions, the oxidation resistance and chemical stability of the SiC fibre were also studied here.

1. Introduction

SiC fibre made from polycarbosilane (PC) possesses high mechanical strength, high heat resistance and other excellent properties. It is flexible enough to be made into various fabrics. It can be used as reinforcements in FRM, FRC, and FRP, and it can also be used as the gap filler between the heat-resisting tiles in the space shuttle [1–4].

SiC fibre has been manufactured on an industrial scale with a trade name of Nicalon® by the Nippon Carbon Co., Tokyo, Japan. It is prepared as follows [5–7]. PC is melt-spun into fibre, cured by pre-heating in air at about 200 °C, and then heat-treated at high temperature in a non-oxidizing atmosphere to give the SiC fibre. The curing process cross-links the PC molecules with oxygen introduced by the pre-heating treatment, which makes the PC fibre infusible. As a result, the SiC fibre made from PC contains considerable amounts of oxygen, which lowers the mechanical properties of the SiC fibre both at room temperature and at high temperatures [8, 9].

We have found that SiC fibre with less oxygen and higher tensile strength can be made by using a polyblend of PC and HTPB as a precursor. In the present work, the reaction of PC with HTPB was studied. On the basis of the results, the preparation of SiC fibre from the PC–HTPB polyblend and the properties of the SiC fibre were investigated in detail.

2. Experimental procedure

2.1. Preparation of PC–HTPB polyblends

PC was synthesized by thermal decomposition of polydimethylsilane at 450 °C for about 10 hours. The number average molecular weight of the PC is 1620.

HTPB was bought from a commercial supplier. Its number average molecular weight is about 3500.

The PC–HTPB polyblend was made by melt-blending of PC and HTPB at 220 °C for 10 minutes using melt-blending equipment built by ourselves. In order to study the reaction of PC with HTPB, the polyblend could also be made at temperatures higher than 260 °C in the melt-blend equipment.

2.2. Preparation of the SiC fibre by using PC–HTPB polyblend as a precursor

The PC–HTPB polyblends were melt-spun into precursor fibres in self-made melt-spun equipment at 200–220 °C. The precursor fibres were cured in air to a certain degree and then heated in a nitrogen gas flow at a heating rate of 150 °C/h to a temperature of 1250 °C for one hour.

2.3. Measurements

The molecular weight distribution was measured using a Waters-244 gel permeating chromatograph (GPC), with 1 ml/min toluene as the eluent.

The differential scanning calorimetry (DSC) curves were obtained by a CDR-1 differential scanning calorimeter by raising the temperature at 10 °C/min up to 400 °C in a nitrogen flow of 20 ml/min.

Thermal gravimetric (TG) analysis was carried out using a WRT-1 TG machine by raising the temperature at 10 °C/min up to 900 °C in a nitrogen flow of 20 ml/min.

Infrared (IR) spectra were measured with a Hitach-270-30 infrared spectrometer by the KBr pellet method.

The mechanical properties of the SiC fibres were measured using a universal testing machine (10 mm gauge length and 2 mm/min cross-head speed at room

0022–2461/91 $03.00 + .12 © *1991 Chapman & Hall*

temperature). The diameters of the fibres were measured using a micrometer.

The densities of the SiC fibres were measured by a liquid displacement method.

Chemical analysis was done for silicon (by a gravimetric method) and carbon (by a combustion volumetric method).

3. Results and discussion

3.1. The reaction of PC with HTPB

When PC and HTPB were melt-blended, they formed one homogeneous phase.

To investigate whether PC could react with HTPB, DSC studies on PC–HTPB polyblend were made. Fig. 1 shows the DSC curves of PC, HTPB and PC–HTPB polyblends. The endothermic peaks of PC–HTPB polyblends at temperatures around 260 °C indicated that reaction between PC and HTPB occurred in this temperature range.

We let specimens of PC, HTPB and PC + 10 wt % HTPB be heated to 260 °C. The GPC curves of the specimens are shown in Fig. 2. The results indicate an increase in the molecular weight of the heat-treated PC + 10 wt % HTPB polyblend. It implied that some combination or condensation reactions had taken place during the heat treatment. In fact, it was observed that PC could react with HTPB to form cross-linked polymers when they were mixed and heated to 260 °C for about one hour.

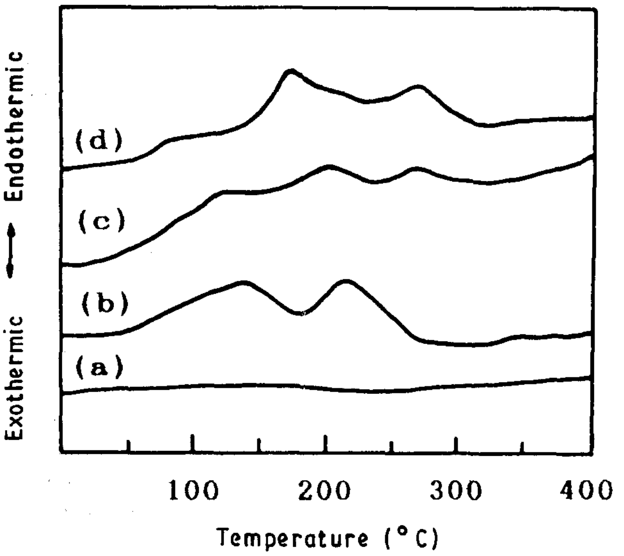


Figure 1 DSC curves of (a) HTPB, (b) PC, (c) PC + 3 wt % HTPB and (d) PC + 30 wt % HTPB.

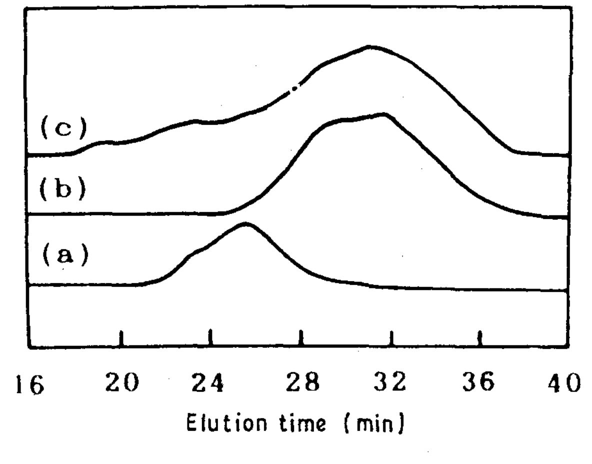
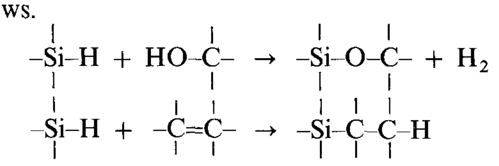


Figure 2 GPC elution curves of (a) HTPB, (b) PC and (c) PC + 10 wt % HTPB.

IR and nuclear magnetic resonance (NMR) spectra analyses demonstrated that Si–H bonds in PC, and –OH groups and C=C bonds in HTPB were involved in the changes. Probably, PC reacts with HTPB as follows.



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{H} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{C}}}- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}- + \mathrm{H_2}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{H} + -\overset{|}{\underset{|}{\mathrm{C}}}=\overset{|}{\underset{|}{\mathrm{C}}}- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{H}$$

3.2. Synthesis of SiC fibres using PC–HTPB polyblends as precursors

The PC–HTPB polyblends were easily melt-spun into precursor fibres, and the precursor fibres were cured in air. Since the PC could react with HTPB to form cross-linked polymers at temperatures around 260 °C, the air-curing process needs only to be carried out to such an extent that the appearance of the PC–HTPB fibre is unchanged below 260 °C. So the oxygen needed for curing PC–HTPB fibre is much less than that needed for curing PC fibre. The cured PC–HTPB fibre was then heated up to 1250 °C in a nitrogen gas atmosphere. As the cross-linking reaction of PC with HTPB had taken place at around 260 °C, the precursor fibre was converted into SiC fibre without collapsing in the process.

Fig. 3 shows the infrared spectra of PC and PC + 10 wt % HTPB fibres before and after curing, and the cured PC + 10 wt % HTPB fibre heat-treated at various temperatures in a nitrogen gas atmosphere. PC fibre showed the characteristic absorption bands of polycarbosilane at 2950 and 2900 $\mathrm{cm^{-1}}$ (C–H), 2100 $\mathrm{cm^{-1}}$ (Si–H), 1400 $\mathrm{cm^{-1}}$ ($\mathrm{Si{-}CH_3}$), 1350 $\mathrm{cm^{-1}}$ ($\mathrm{Si{-}CH_2{-}Si}$), 1250 $\mathrm{cm^{-1}}$ ($\mathrm{Si{-}CH_3}$), 1020 $\mathrm{cm^{-1}}$ (Si–O–Si, Si–O–C, $\mathrm{Si{-}CH_2{-}Si}$), and 820 $\mathrm{cm^{-1}}$ ($\mathrm{Si{-}CH_3}$). The 3450 and 1620 $\mathrm{cm^{-1}}$ bands were attributed to the stretching and deformation vibrations of absorbed water molecules, respectively. In the IR spectrum of cured PC fibre, the decrease in absorption peaks at 2100 $\mathrm{cm^{-1}}$ and 1250 $\mathrm{cm^{-1}}$ was remarkable, and the absorption peaks at 3680 $\mathrm{cm^{-1}}$ (free O–H stretching) and 1710 $\mathrm{cm^{-1}}$ (C=O stretching) were also observed. A strong absorption at 1020 $\mathrm{cm^{-1}}$ indicated that oxygen had been introduced in the PC fibre. The IR spectrum of PC + 10 wt % HTPB fibre not only showed the characteristic absorption bands of PC, but also showed the absorption bands of HTPB at 3070, 1660 and 965 $\mathrm{cm^{-1}}$ (RHC=CHR′) and 1470 $\mathrm{cm^{-1}}$ ($\mathrm{-CH_2-}$). After curing, the decrease in absorption peaks at 2100 $\mathrm{cm^{-1}}$ and 1250 $\mathrm{cm^{-1}}$ were much less than that in PC fibre and the absorption peaks at 3680 $\mathrm{cm^{-1}}$ (O–H) and 1710 $\mathrm{cm^{-1}}$ (C=O) were also observed, but the peaks were much smaller than those in cured PC fibre. The increase in absorption at 1020 $\mathrm{cm^{-1}}$ is only small. It can be seen that the oxygen

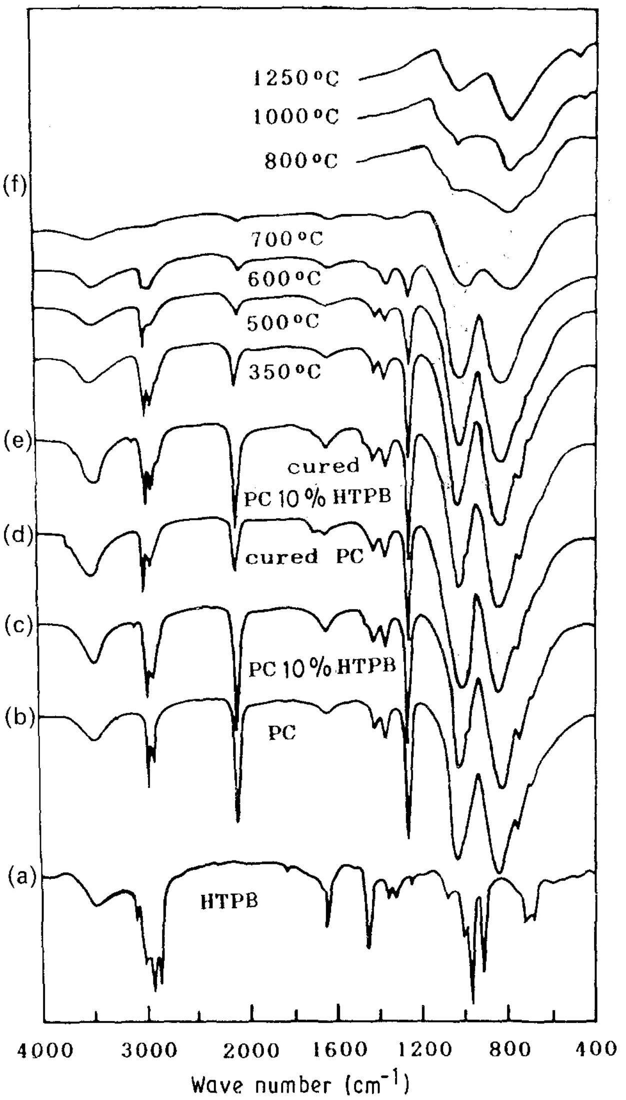


Figure 3 Infrared spectra of (a) HTPB, (b) PC fibre, (c) PC + 10 wt % HTPB fibre, (d) cured PC fibre, (e) cured PC + 10 wt % HTPB fibre and (f) the cured PC + 10 wt % HTPB fibre heat-treated at a temperature in the range of 350 to 1250 °C in nitrogen flow.

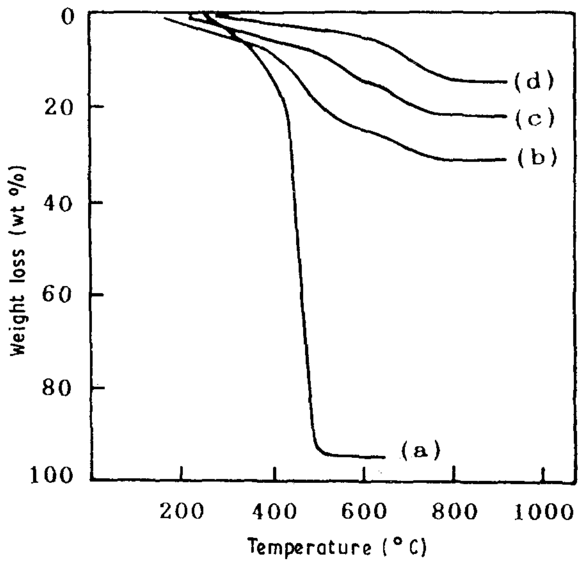


Figure 4 TG curves of cured (a) HTPB, (b) PC + 20 wt % HTPB fibre, (c) PC + 5 wt % HTPB fibre and (d) PC fibre.

TABLE I The weight loss of cured precursor fibres after heat-treatment at 1250 °C

Precursor fibres	PC	PC + 5 % HTPB	PC + 10% HTPB	PC + 15% HTPB
weight loss (wt %)	21.4	26.7	30.0	34.0
weight loss due to HTPB (wt %)	0	5.3	9.0	12.6

introduced into the PC–HTPB fibre is much less than that in PC fibre.

After the cured PC–HTPB fibre has been heat-treated at 350 °C, the absorption peak at 2100 cm^{-1} largely decreased and the absorption peaks at 3070, 1660 and 965 cm^{-1} were dispelled due to the reaction of Si–H bonds with C=C bonds. As the heat-treatment temperature exceeded 500 °C, thermal decomposition of the side chains such as Si–H, Si–CH_3 and C–H in Si–CH_2–Si occurred. The infrared spectrum of the fibre heat-treated at 700 °C showed that the absorptions due to the Si–H and Si–CH_3 were dispelled. When the temperature was above 700 °C, the PC–HTPB fibre was gradually converted into SiC fibre. The infrared spectra of the fibre heat-treated at 1250 °C was very similar to those of commercial α- and β-SiC. The absorption bands at 1090 cm^{-1} (Si–O) and 820 cm^{-1} (Si–C) were clearly separated.

The TG curves of PC, HTPB and PC–HTPB polyblends in nitrogen flow are shown in Fig. 4. HTPB decomposed readily at 400–500 °C, and it almost totally decomposes into lower molecular weight components at above 500 °C. While the pyrolysis process of the cured PC fibre mainly occurred at 600–750 °C, the TG curves of cured PC–HTPB fibres were different from those of PC and HTPB. As a result of the reaction between PC and HTPB, the weight loss of cured PC–HTPB fibres increased gradually with the rise in heat-treatment temperature up to 750 °C. The more HTPB a polyblend fibre contained, the higher was the weight loss in the heat treatment process.

Table I shows the weight loss of the cured PC and PC–HTPB fibres after heat-treatment at a heating rate of 150 °C/h to a temperature of 1250 °C for one hour. It can be seen that, after heat-treatment at 1250 °C, the elements of HTPB almost totally escaped.

3.3. The properties of the SiC fibre

The chemical compositions of the SiC fibres are shown in Table II. It can be seen that the SiC fibres obtained from PC–HTPB polyblends contain less oxygen.

The tensile strengths and densities of the SiC fibres obtained from PC–HTPB polyblends vary with the HTPB content in the precursor fibres, as shown in Table III. It is interesting to note that the tensile strength of the SiC fibre can be improved by using a polyblend of PC and an appropriate amount of HTPB as a precursor. We have found that the tensile strength of the SiC fibre obtained from PC + 3% HTPB polyblend is the highest. It is increased by 26% compared with that obtained from PC. The increase in tensile strength is considered to be due to the decrease in

TABLE II The chemical compositions of the SiC fibres

SiC fibres	Si(wt %)	C(wt %)	O(wt %)^a
PC SiC fibre	53.72	29.10	17.18
PC + 3 % HTPB SiC fibre	53.64	33.04	13.32
PC + 5 % HTPB SiC fibre	55.27	34.40	10.33
PC + 10 % HTPB SiC fibre	54.96	36.11	8.93

^{a}O(wt %) = 100% − (Si% + C%).

TABLE III The relation between HTBP content and the tensile strength and density of the SiC fibres

HTPB content (wt %)	0	1	3	5	10	15
mean diameter (μm)	10.7	8.7	8.6	7.9	10.2	13.0
mean strength (MPa)	1773	1688	2244	2034	1909	1598
apparent density (g/cm^3)	2.43	2.44	2.42	2.41	2.39	2.36

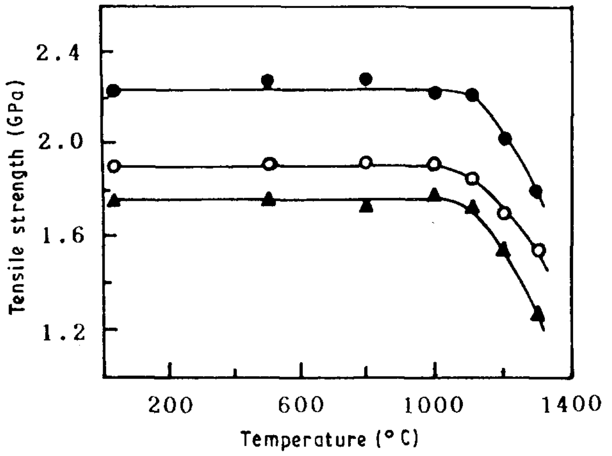


Figure 5 The tensile strength of (▲) PC SiC fibre, (○) PC + 10 wt % HTPB SiC fibre and (●) PC + 3 wt % HTPB SiC fibre by heating in air at various temperatures for one hour.

oxygen content in the SiC fibre. When the HTPB content is above 3 wt %, the tensile strength of the SiC fibre decreases. This decrease in tensile strength may be attributed to the presence of flaws that are produced as a result of evaporation of lower molecular weight components during heat treatment. As noted above, the weight loss increases with the increase in HTPB content.

The densities of the SiC fibres decrease with the increase of HTPB content in the precursor fibres. This decrease can also be attributed to the evaporation of lower molecular weight components during heat treatment.

The surface of the SiC fibres obtained from PC–HTPB polyblends is very smooth, just like that from PC. The X-ray diffraction patterns of the SiC fibres made from PC–HTPB polyblends show that the SiC fibres are composed of superfine crystallites of β-SiC. The crystallinity of the SiC fibre decreased with the increase in HTPB content in the precursor fibre. The SiC fibres made from PC–HTPB polyblends contain only silicon, carbon and oxygen in the form of silicon carbide, silicon oxide and free carbon.

The SiC fibres made from PC–HTPB polyblends possess excellent oxidation resistance up to 1200 °C, as shown in Fig. 5.

The chemical stability of the SiC fibres obtained from PC–HTPB polyblends were tested by immersing the fibres into solutions of 20% HCl, 50% HNO_3, 50% H_2SO_4 and 20% NaOH at 80 °C for more than 24 hours. In each case no reaction occurred. The weights and the tensile strengths of the fibres were almost unchanged; apparently, the SiC fibres possess very good chemical stability.

4. Conclusions

The PC–HTPB polyblends were made by melt-blending of PC and HTPB. PC–HTPB polyblends form one homogeneous phase. They can easily be melt-spun into precursor fibres.

When PC–HTPB polyblends were heated to temperatures around 260 °C, the Si–H bonds in PC react with O–H and C=C bonds in HTPB to form cross-linked polymers. So HTPB in the precursor fibre can be used as a curing agent. As a result, SiC fibre with low oxygen content and higher tensile strength can be synthesized from a PC–HTPB polyblend.

SiC fibre obtained from PC–HTPB polyblends is a uniform cohesion of superfine β-SiC particles. It contains only silicon, carbon and oxygen. The SiC fibres possess excellent oxidation resistance up to 1200 °C, and they also possess very good chemical stability.

References

1. H. ICHIKAWA, F. MACHINO, T. ISHIKAWA, K. OKAMURA and Y. HASEGAWA, *J. Mater. Sci.* **21** (1986) 4352.
2. G. SIMON, A. R. BUNSELL, *ibid.* **19** (1984) 3649.
3. T. MAH, N. L. HECHT, D. E. McCULLUM, J. R. HOENIGMAN, H. M. KIM, A. P. KATZ and H. A. LIPSITT, *ibid.* **19** (1984) 1191.
4. T. ISHIKAWA, "Future trends in SiC fibre-reinforced materials", IUPAC CHEMRAWN VI, Tokyo (1987) T21.
5. S. YAJIMA, *Phil. Trans. R. Soc. Lond.* **A294** (1980) 419.
6. Y. HASEGAWA, M. IIMURA and S. YAJIMA, *J. Mater. Sci.* **15** (1980) 720.
7. S. YAJIMA, Y. HASEGAWA, K. OKAMURA and T. MATSUZAWA, *Nature* **273** (1978) 525.
8. K. OKAMURA, M. SATO and Y. HASEGAWA, *J. Mater. Sci. Lett.* **2** (1983) 769.
9. K. OKAMURA, M. SATO, T. MATSUZAWA and Y. HASEGAWA, *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) **25** (1984) 6.

Received 13 July 1989
and accepted 6 June 1990