

Si-C Fiber Prepared from Polycarbosilane Cured Without Oxygen

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A new curing method for polycarbosilane was developed. In this method, halogenated hydrocarbon or unsaturated hydrocarbon vapor was used as curing agent. Si-C fiber with a small amount of oxygen was prepared from polycarbosilane fiber cured without introducing oxygen. The structure and the properties of the fiber are discussed in comparison with Si-C-O fiber obtained from thermal-oxidized polycarbosilane fiber. Using the new curing method, the thermal stability of the Si-C fiber was far improved with respect to that of conventional Si-C-O fiber.

KEY WORDS: Si-C fiber; polycarbosilane; curing method; thermal stability.

INTRODUCTION

Polycarbosilane has been used as a precursor for Si-C ceramics, particularly for continuous SiC fiber. Commercial SiC fiber is produced in the following process. First polycarbosilane is melt-spun, then the resulting fiber bundle is cured by heating in air. The cured fiber is then heat-treated under an inert atmosphere. Oxygen, introduced by curing, affects the thermal stability of the fiber. For example, the strength is decreased by crystallization of cristobalite and grain growth of β -SiC characterized by the evolution of CO gas [1, 2]. Accordingly, for the purpose of utilizing SiC fiber as reinforcements in many ceramic matrix composites, development of oxygen-free Si-C fiber is necessary. Recently, Si-C-O fiber with a small amount of oxygen was prepared from polycarbosilane fiber cured by electron beam irradiation [3]. It was shown that this fiber had improved thermal stability.

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In the present research, a new curing method for polycarbosilane has been studied. In this method, halogenated hydrocarbon vapor or unsaturated hydrocarbon vapor was used as a curing agent. The possibility of improving the thermal stability of the Si-C-O fiber by using this curing method has been established.

EXPERIMENTAL

Polycarbosilane (PC), which consists of $\text{SiC}_4 = 0.55$, $\text{SiC}_3\text{H} = 0.45$, and $\text{SiC}_x\text{Si}_{4-x} = 0$ [4], was synthesized by thermal decomposition and condensation of poly(dimethylsililene). The number-average molecular weight was 2060. PC was melt-spun at 345°C . The resulting fiber bundle was cured by heating in a tubular furnace (30 mm in diameter) up to a specific temperature at a rate of $10^\circ\text{C} \cdot \text{h}^{-1}$ in nitrogen gas flow containing carbon tetrachloride, CCl_4 , chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$, and cyclohexene, C_6H_{10} , vapor, and then kept at this temperature (hereafter, referred to simply as T_c , the curing temperature) for 1 h. The curing gas flow was prepared by mixing dried nitrogen (at $50 \text{ cm}^3 \cdot \text{min}^{-1}$) with dried nitrogen (at $10\text{--}20 \text{ cm}^3 \cdot \text{min}^{-1}$) that was bubbled through the liquid hydrocarbon at room temperature. A schematic diagram of the curing apparatus is shown in Fig. 1.

The cured fiber was then heat-treated in a tubular furnace (42 mm in diameter) up to a specific temperature at a rate of $100^\circ\text{C} \cdot \text{h}^{-1}$ in a dried nitrogen or argon gas flow (at $100 \text{ cm}^3 \cdot \text{min}^{-1}$) and, finally, kept at this temperature for 1 h. Average diameters of the Si-C fibers were within the range of $8\text{--}14 \mu\text{m}$.

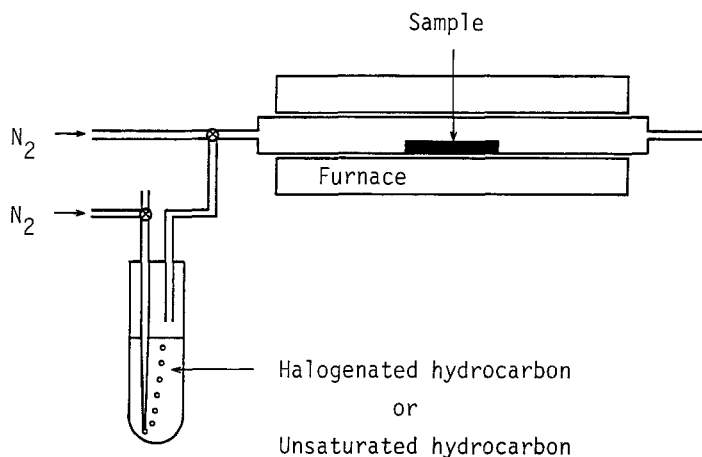


Fig. 1. A schematic diagram of the curing apparatus.

PC powder was heat-treated in a nitrogen gas flow containing CCl_4 vapor at temperatures ranging from 80 to 220°C for 21.5 h, and then the weight gain and the ceramic yield at 1200°C in argon gas flow were measured.

PC, CCl_4 vapor, and PC in CCl_4 vapor were studied by means of pyrolysis-gas chromatography. The degradation of them was carried out in a tubular furnace (24 mm in diameter) up to 600°C at a rate of $2^\circ\text{C} \cdot \text{min}^{-1}$ in helium gas flow (at $30 \text{ cm}^3 \cdot \text{min}^{-1}$).

Mechanical properties of fibers were measured in a universal testing machine at room temperature with a 25-mm gauge length for 30 filaments, the average values being taken.

RESULTS AND DISCUSSION

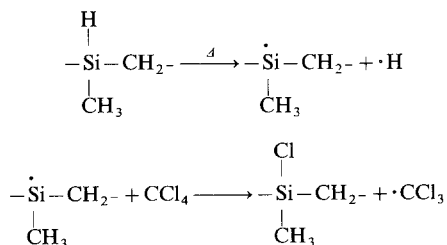
Curing Mechanism

Figure 2 shows infrared difference spectra of PC fibers before and after CCl_4 curing ($T_c = 200^\circ\text{C}$) and C_6H_{10} curing ($T_c = 300^\circ\text{C}$). It is clear that the absorbances of the Si-H, C-H, and Si- CH_3 bonds decreased. The Si-H bonds almost disappeared and Si-Cl bonds appeared on CCl_4 curing. The number-average molecular weights of CCl_4 -cured and C_6H_{10} -cured PC were 1.4 and 1.9 times that of uncured PC, respectively.

The weight gain of PC powder reacted with CCl_4 vapor at various temperatures for 21.5 h and the ceramic yield of the pyrolysis product at 1200°C are shown in Fig. 3. These results indicate that PC reacted with CCl_4 at about 100°C . The weight gain is attributable to the formation of Si-Cl bonds.

Figure 4 shows pyrograms obtained with PC, CCl_4 vapor, and PC in CCl_4 vapor up to 600°C . It is apparent that PC indicated the reaction with CCl_4 at a temperature (about 180°C) lower than that of the degradation of CCl_4 vapor or PC, that is, about 400°C .

From the above results, it is assumed that the reaction of PC with CCl_4 vapor is caused by silyl radicals which have been reported in the reaction of hydrosilanes with CCl_4 in solution [5]:



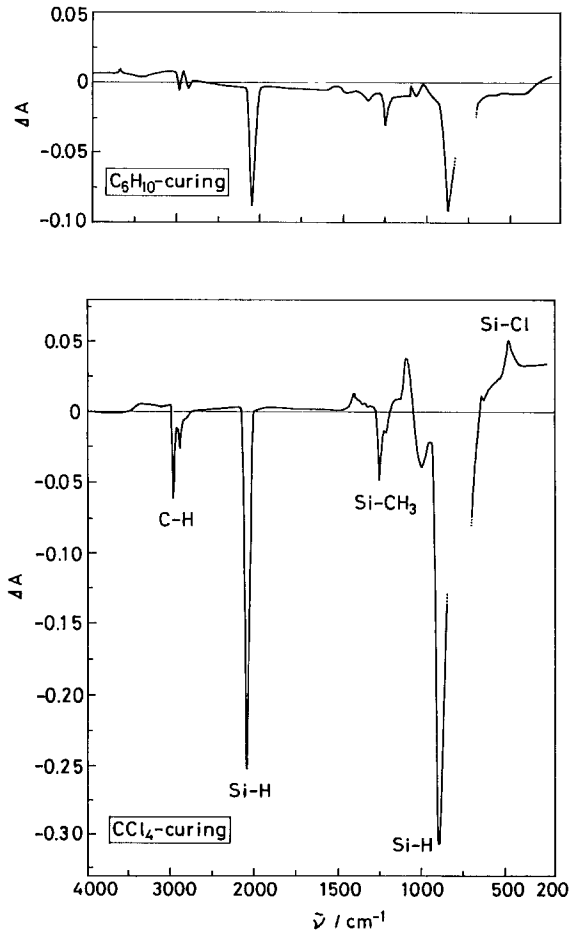
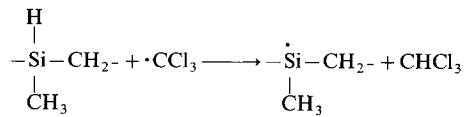
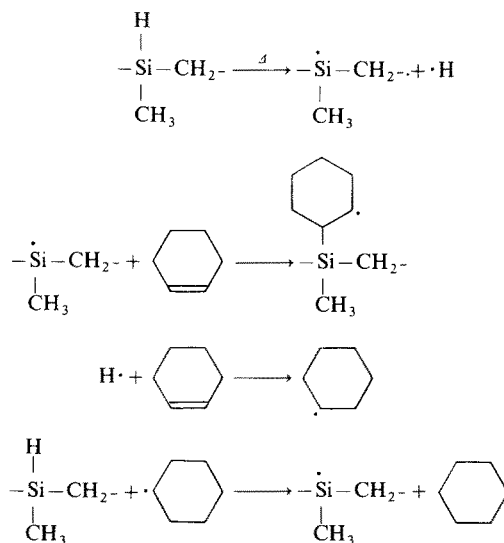


Fig. 2. Infrared difference spectra of PC before and after CCl₄ and C₆H₁₀ curing.



The reaction of PC with cyclohexene vapor is assumed to be as follows:



The radicals formed in the above reactions appear to undergo further reactions which may be complex, resulting in cross-linking between PC molecules.

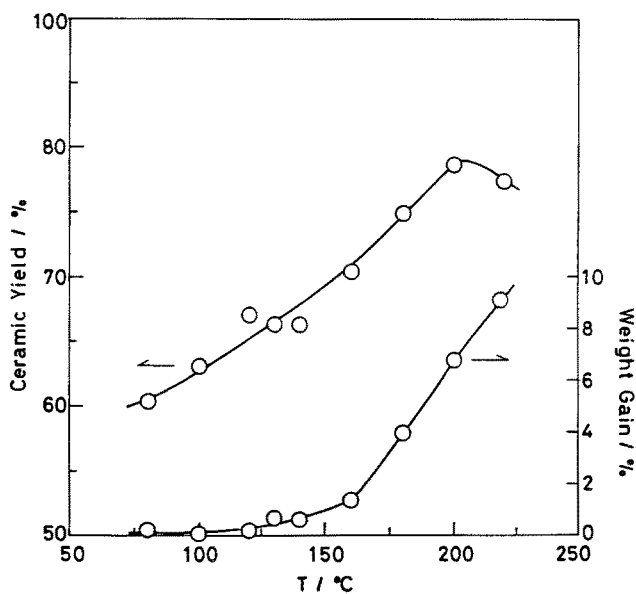


Fig. 3. Weight gain of PC reacted with CCl_4 vapor at various temperatures for 21.5 h and ceramic yield of the cured PC heat-treated at 1200°C in argon.

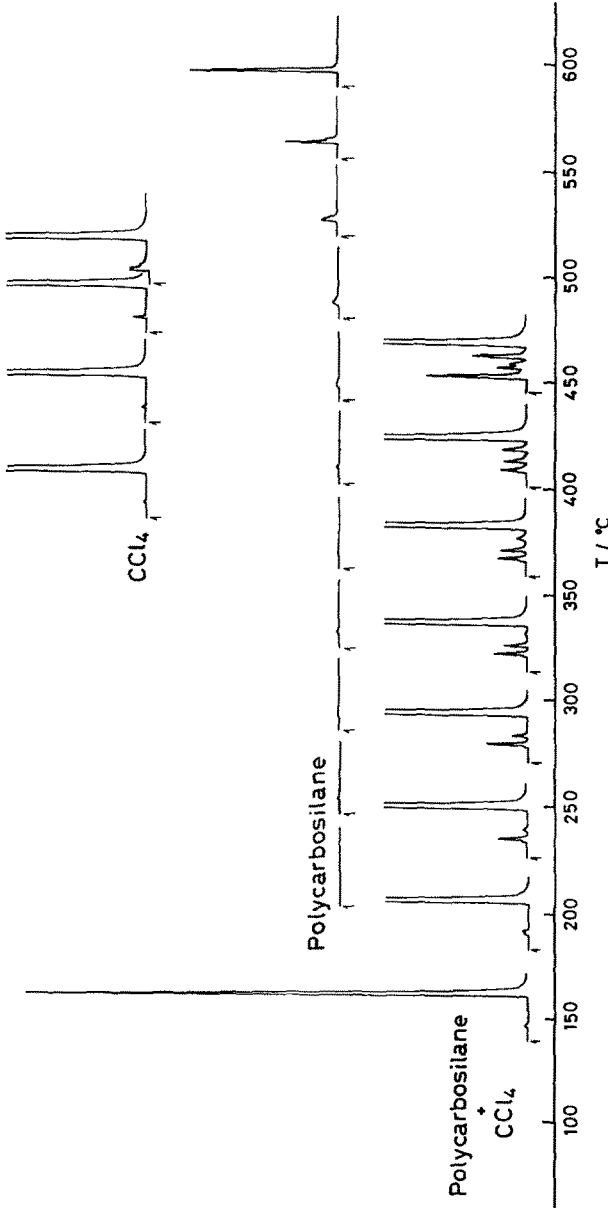


Fig. 4. Change of pyrograms of PC, CCl₄ vapor, and PC in CCl₄ vapor during pyrolysis up to 600°C at a rate of 2°C·min⁻¹ in helium gas flow. The pyrolysates were separated on a 1 m × 3-mm-I.D. Stainless-steel column packed with 10% SE-30 on Chromosorb W (80-100 mesh) and detected with a thermal conductivity detector.

Si-C Fiber

Tensile strength of Si-C fibers in comparison with that of Si-C-O fibers obtained by thermal-oxidation curing [2] is shown in Fig. 5 as a function of the heat-treatment temperature. It appears that the thermal stability of Si-C fibers is higher than that of Si-C-O fibers. However, a decrease in strength took place distinctly above 1500°C even in the Si-C fibers. This decrease in strength is probably related to the small amount of oxygen in the fiber [3]. Oxygen analysis showed the oxygen content in the Si-C fiber obtained by CCl_4 curing and heat treatment at 1400°C in a dried argon gas flow to be 2.38 wt%.

Tensile strengths of Si-C and Si-C-O fibers are shown in Fig. 6 as a function of β -SiC crystalline size (L_{111}). From these results, the influence of L_{111} on the strength of the fiber is evident. On the other hand, the fibers

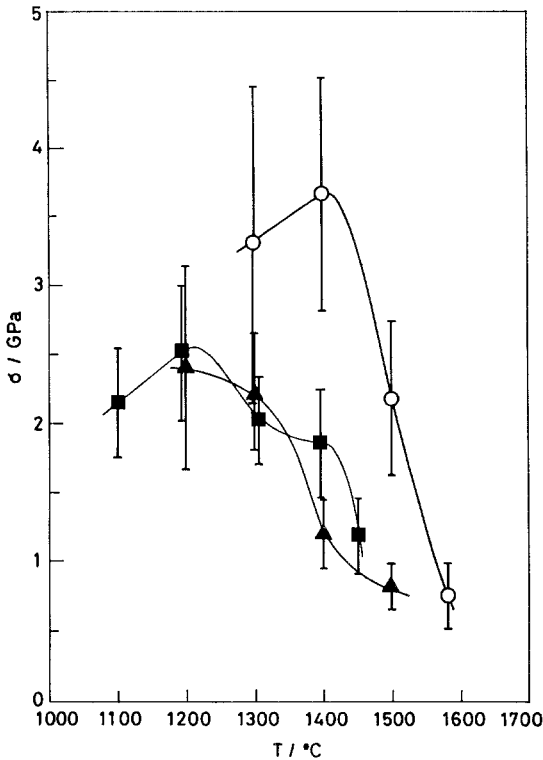


Fig. 5. The relation between heat-treatment temperature and tensile strength of Si-C fiber and Si-C-O fiber (2). (○) C_6H_{10} curing, heat-treated in N_2 ; (▲) thermal-oxidation curing, heat-treated in N_2 ; (■) thermal-oxidation curing, heat-treated in vacuum.

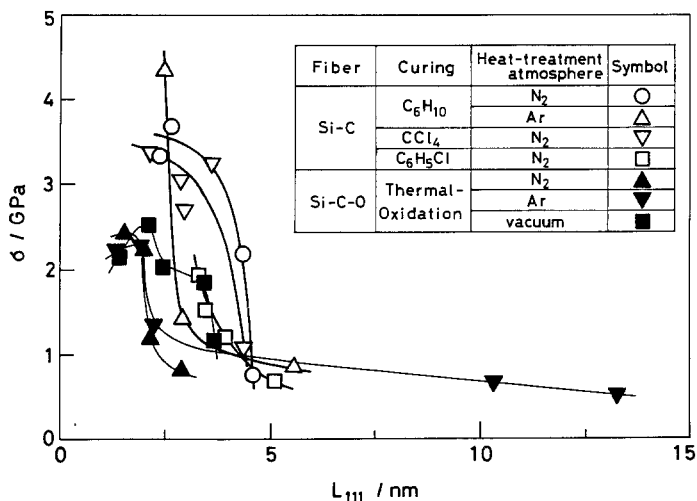


Fig. 6. Tensile strength of Si-C fiber and Si-C-O fiber as a function of β -SiC crystalline size (L_{111}).

having the same L_{111} value have different strengths, depending upon the curing method and heat-treatment conditions.

These results show that the thermal stability of Si-C fiber must be improved by both depression of crystallization of β -SiC and controlling the composition of the fiber, that is, the carbon, oxygen, and nitrogen content in the fiber.

CONCLUSION

A new curing method for polycarbosilane was developed. In this method, halogenated hydrocarbon vapor or unsaturated hydrocarbon vapor was used as a curing agent to make polycarbosilane fiber infusible without introducing oxygen.

Using this curing method, the thermal stability of Si-C fiber was far improved with respect to that of a conventional SiC fiber.

In the future, the curing mechanism will be studied further and the relation between fiber strength and the crystalline size or fiber composition will be discussed in detail.

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