

# Dissolution of Oxidation-Cured Poly(carbosilane) Fiber into Polar Organic Solvents

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**ABSTRACT:** The solubility of oxidation-cured polycarbosilane (PCS) fiber into benzene, tetrahydrofuran (THF), acetone, and ethanol was investigated. The solubility of the fiber in benzene and THF decreases as the curing temperature increases. The fiber cured at 433–463 K, however, shows higher solubility in acetone and ethanol than the original fiber and the fiber cured at 473 K. The remaining gels in benzene and THF keep their fibrous shape, while in acetone and ethanol often appear as swollen gels.

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**Key words:** poly(carbosilane); oxidation curing; ceramic precursor polymer; solubility

## INTRODUCTION

Solubility and fusibility of organosilicon polymers have been an important issue in the development and application of organosilicon polymers. It is well known that the first substituted silane polymer, polydiphenylsilane and polydimethylsilane, which were synthesized several years ago,<sup>1,2</sup> had been poorly characterized and elicited little scientific interest for a long time because of their lack of processability. Polycarbosilane (PCS), which is synthesized from the infusible polydimethylsilane, is fusible and soluble to hexane, benzene, and tetrahydrofuran (THF). A melt phase of this polymer can be spun into fiber and is now used as the precursor to synthesize silicon carbide fibers.<sup>3,4</sup> A curing process, however, is necessary to permit the conversion of PCS fiber to silicon carbide (SiC) fiber without softening during heat treatment. Several types of curing processes have been developed, but oxidation-curing, which is currently used in an industrial scale, is popular.<sup>5–8</sup>

Ichikawa in Nippon Carbon Co., Ltd (NCK) has demonstrated that the oxidation curing decreases the solubility of the PCS fiber in hexane and THF.<sup>9</sup> Recently, we found that the oxidation-cured PCS fiber can be dissolved into polar organic solvents such as acetone and ethanol, although the original PCS without the curing does not have high solubility in polar solvents. The aim of this article is to report the solubility of oxidation-cured fiber in organic solvents as a function of the curing temperature and to demonstrate the possibility of controlling the polarity of the carbosilane polymers, which has been used as a precursor of silicon carbide ceramics.

## EXPERIMENTAL

### Material

The original polycarbosilane (PCS) was supplied from Shin-Estu Chemical Co., Ltd. (Tokyo, Japan), and spun into fiber form having a 20  $\mu\text{m}$  diameter. The prepared fiber was cured in a  $\text{O}_2$  gas flow at a temperature of up to 433–473 K.

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The heating rate was 30 K/h, and the holding time was 0.5 h. The precured PCS fiber supplied from NCK, which is a precursor of commercialized silicon carbide fibers, was also prepared. The diameter of the fibers are 15  $\mu\text{m}$ . Benzene, THF, acetone, and ethanol (Super Special Grade of Wako Chemicals, Osaka, Japan) were used soon after opening caps of vials without further purification.

### Estimation of Gel Fractions

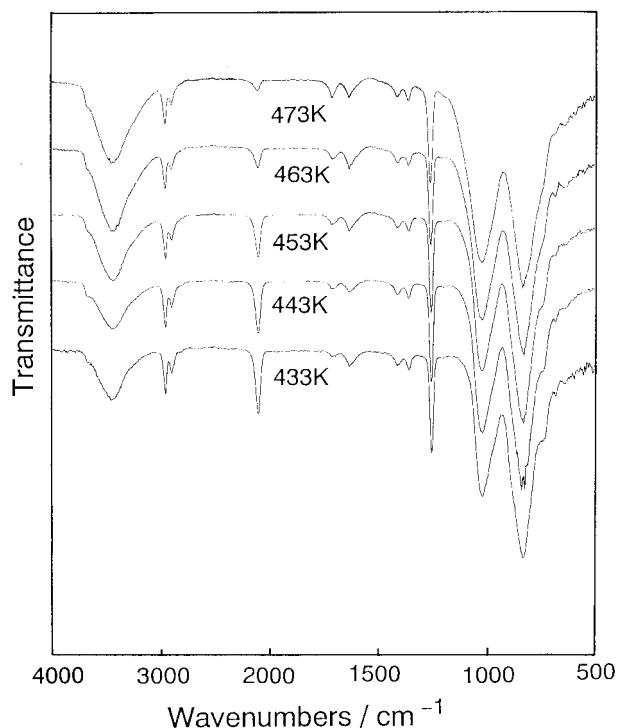
50–100 mg of the cured fiber was put into glass tubes and immersed in 10 mL of organic solvents with gentle shaking. After standing at room temperature for 1 h, the solutions in the tubes were centrifuged at 2000 rpm to separate gels from the solutions. Gel fractions were estimated from the residual weight ratios of gels dried under reduced pressure.

### Measurements

The infrared (IR) spectra in the range of 4000–500  $\text{cm}^{-1}$  were obtained by the KBr pellet method (Perkin Elmer, FT-IR1600). Thermogravimetric analysis (TGA) were performed in a platinum crucible on 3–5 mg of sample under a flow of pure argon gas with a heating rate of 20 K/min (Rigaku, TG-8110). The morphology of the separated gels were observed by scanning electron microscopy (SEM) (Hitachi, FE SEM S-4500) after drying and pyrolyzing the gels at 1273 K.

## RESULTS AND DISCUSSION

After the oxidation curing, the weight of the fiber increased 2.8, 6.6, 8.2, 13.7, and 14.9% at the curing temperature of 433, 443, 453, 463 and 473 K. Figure 1 shows the IR spectra of these oxidation-cured PCS fibers. The IR spectra exhibited the absorption bands of the SiO—H stretching (3450  $\text{cm}^{-1}$ ), C—H stretching (2950–2900  $\text{cm}^{-1}$ ), Si—H stretching (2100  $\text{cm}^{-1}$ ), C=O stretching (1710  $\text{cm}^{-1}$ ), CH<sub>2</sub> deformation (1400  $\text{cm}^{-1}$ ), Si—CH<sub>3</sub> deformation (1250  $\text{cm}^{-1}$ ), CH<sub>2</sub> wagging in Si—CH<sub>2</sub>—Si (1020  $\text{cm}^{-1}$ ), and Si—CH<sub>3</sub> rocking or Si—C stretching (820  $\text{cm}^{-1}$ ). As the curing temperature increases, the Si—H stretching band at 2100  $\text{cm}^{-1}$  apparently decreases, and the Si—O—Si band at about 1100  $\text{cm}^{-1}$  begins to

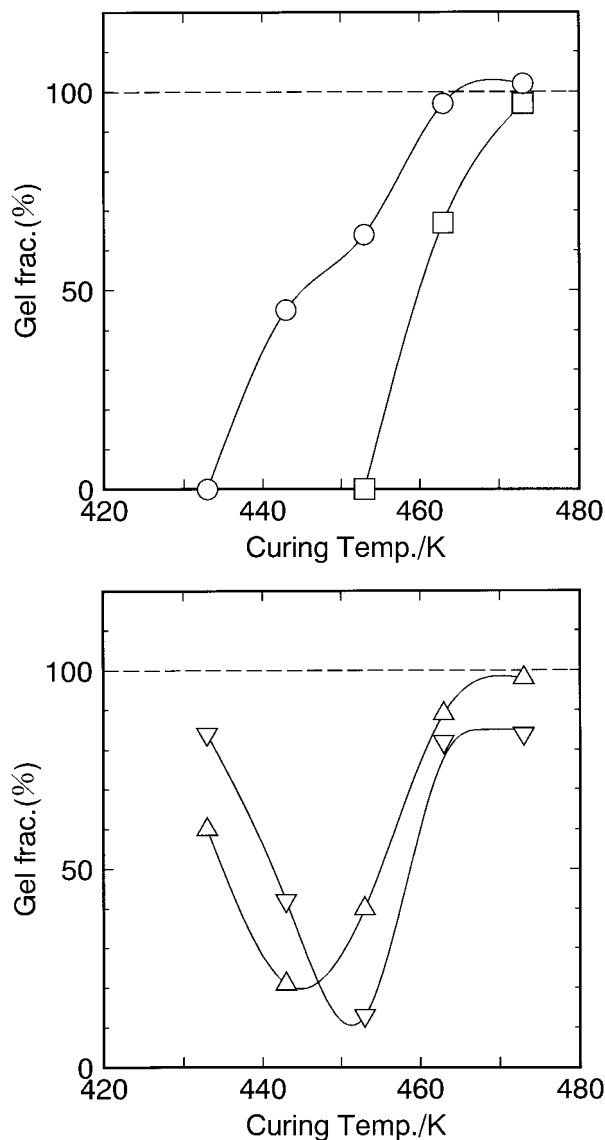


**Figure 1** IR spectra of oxidation-cured PCS fibers.

overlap on the original PCS spectrum. Intensity of SiO—H broad band also increases.<sup>5</sup>

Figure 2 shows the change in gel fraction of the fibers with an increase of the curing temperature. The original PCS is soluble in benzene and THF but only 20% soluble in acetone and quite insoluble in ethanol. A gel fraction appears at a curing temperature of 443 K in benzene and at 463 K in THF. THF should be a better solvent for PCS than benzene. In both solvents, the gel fraction increases as the curing temperature increases. On the other hand, the cured fiber shows abnormal solubility in acetone and ethanol at the curing temperature from 433 to 473 K. The solubility in acetone shows a minimum at 443 K, while that in ethanol shows a minimum at 453 K. Immersion in ethanol yields 20% of the soluble component from the fiber, even at the curing temperature of 473 K.

In order to investigate the characters of the remaining gels and the soluble components, 200–300 mg of the precured precursor fiber was immersed in organic solvents to separate out the gel fraction and soluble component from the fiber. The IR spectrum of this precured fiber is similar to the PCS fiber oxidation-cured at 453 K in our laboratory, but the diameter is thinner. The mea-



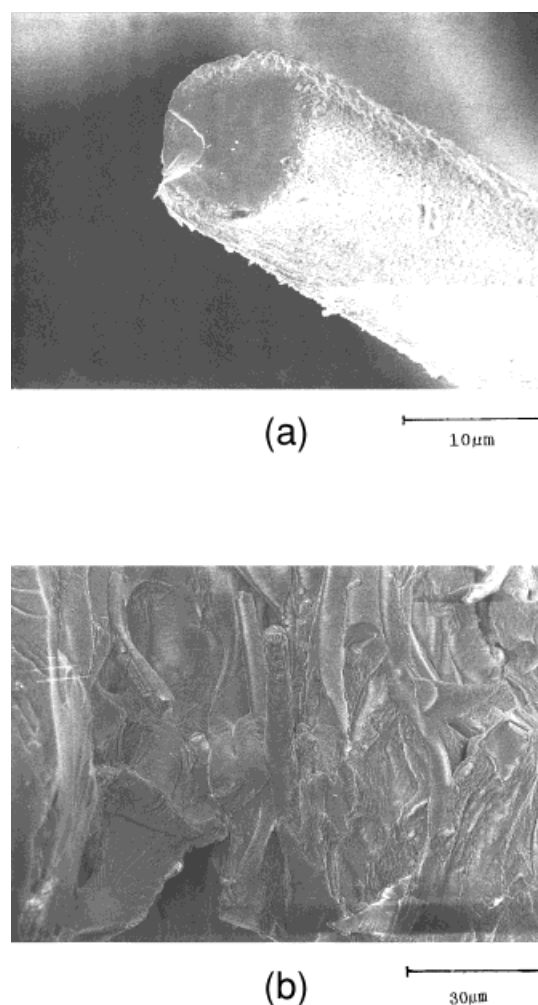
**Figure 2** The results of immersion tests of oxidation-cured PCS fibers in organic solvents: (a) immersion in benzene ( $\circ$ ) and THF ( $\square$ ) for 1 h; (b) immersion in acetone ( $\triangle$ ) and ethanol ( $\nabla$ ) for 1 h.

sured gel fractions are 79, 47, 29, and 42% in benzene, THF, acetone, and ethanol, respectively.

The shape of gels is also dependent on the kind of the immersion solvents. The gel in benzene is white and keeps its fibrous shape, while the gel in THF is quasitransparent and partially keeps its fibrous shape. The gels in acetone and ethanol appear as quasitransparent swelled slime. The SEM photographs of the gels separated out from the original precured fiber in benzene and ethanol are shown in Figure 3. The samples were suffi-

ciently dried and pyrolyzed at 1273 K before the SEM observations. The gel in benzene was the aggregate of the short column of the fibers. After the elimination of the soluble components, the surface of the fiber is slightly roughed; but the core of the fiber shows no indication of degradation. On the other hand, the gel in ethanol does not keep the independent shape. Only the trace of the fibrous shape is observed in the bulk gel aggregate. The fiber immersed in ethanol is considered to be perfectly fused with swelling.

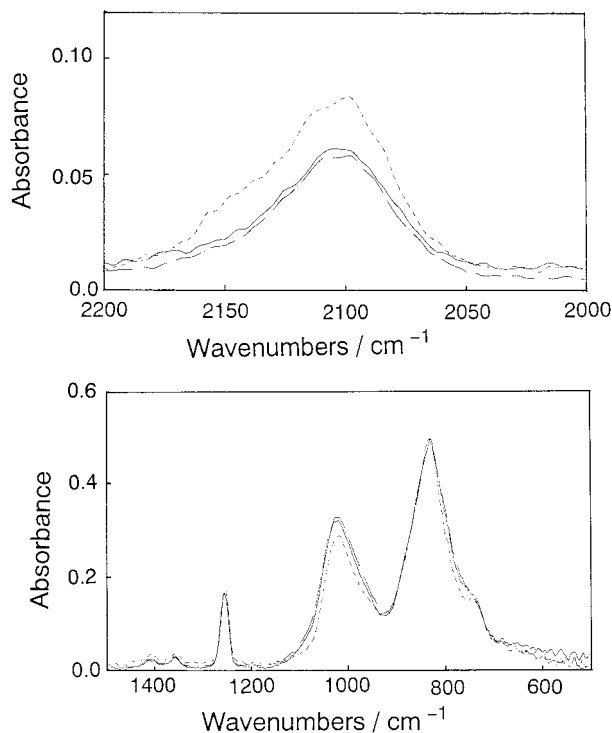
Figure 4 shows the expanded IR spectra of the original fiber, the gel fraction, and the soluble component in benzene between 2200–2000 and 1500–500  $\text{cm}^{-1}$ . The longitudinal axis is represented by absorbance. Intensity of the peaks are



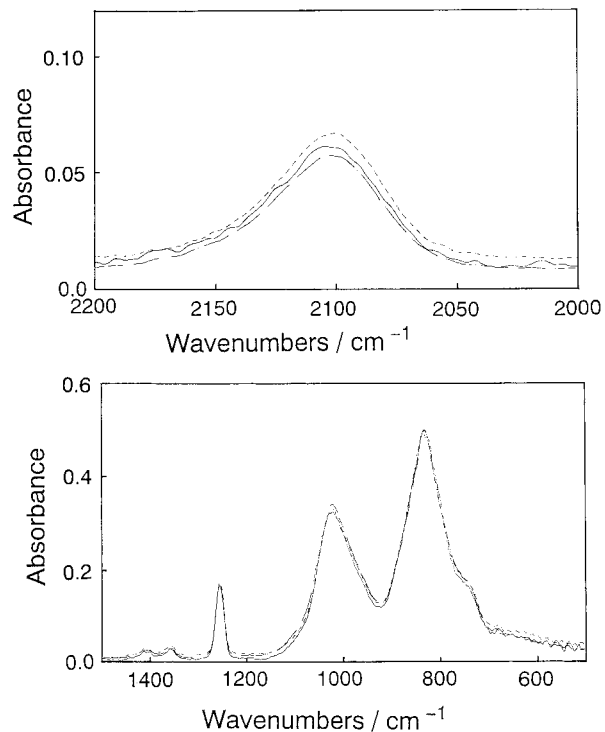
**Figure 3** SEM photographs of the gels obtained from precured PCS fiber after pyrolysis at 1273 K: (a) gel in benzene after 1 h of immersion; (b) gel in ethanol after 1 h of immersion.

normalized by the absorption band at  $820\text{ cm}^{-1}$  as 0.5. These IR spectra indicate that the gel fraction is poor in Si—H and rich in the Si—O—Si bond, while the soluble component is rich in the Si—H bond and poor in the Si—O—Si. TGA—differential thermal analysis (DTA) analysis revealed that the residual weight of the dried gel after  $1273\text{ K}$  pyrolysis was 85%, which was same as the residual weight of the original precured fiber after pyrolysis. The main weight losses occurred at  $500\text{--}750$  and  $800\text{--}1100\text{ K}$ , which had been respectively assigned to the  $\text{H}_2\text{O}$  gas evolution with exothermic reaction and the  $\text{CH}_4$  gas evolution with endothermic reaction.<sup>10,11,12</sup> The residual weight after pyrolysis of the benzene soluble component was, however, decreased to 75%. The main weight losses occurred at the similar temperature regions to those of the original precured fibers.

Figure 5 shows the expanded IR spectra of the



**Figure 4** Expanded IR spectra of the gel and soluble component from precured PCS fiber in benzene. (a) IR spectra from  $2200$  to  $2000\text{ cm}^{-1}$  normalized by the absorption at  $820\text{ cm}^{-1}$  as 0.5: (—, cured PCS fiber; - · - · -, gel fraction; - - - - -, soluble component). (b) IR spectra from  $1500$  to  $500\text{ cm}^{-1}$  normalized by the absorption at  $820\text{ cm}^{-1}$  as 0.5: (—, cured PCS fiber; - · - · -, gel fraction; - - - - -, soluble component).



**Figure 5** Expanded IR spectra of the gel and soluble component from precured PCS fiber in ethanol. (a) IR spectra from  $2200$  to  $2000\text{ cm}^{-1}$  normalized by the absorption at  $820\text{ cm}^{-1}$  as 0.5: (—, cured PCS fiber; - · - · -, gel fraction; - - - - -, soluble component). (b) IR spectra from  $1500$  to  $500\text{ cm}^{-1}$  normalized by the absorption at  $820\text{ cm}^{-1}$  as 0.5: (—, cured PCS fiber; - · - · -, gel fraction; - - - - -, soluble component).

fiber, the gel fraction, and the soluble component in ethanol. The Si—H absorption band in the soluble component is a little higher than that in the gel, but the Si—O—Si band at about  $1100\text{ cm}^{-1}$  shows no differences in these three samples. The TGA—DTA analysis revealed that the residual weights of the gel and the soluble component after the heat treatment at  $1273\text{ K}$  were absolutely the same as that of the original precursor fiber.

## CONCLUSIONS

From the data reported in this article, the dissolution of oxidation-cured PCS fibers in polar organic solvents is confirmed. The dissolution behavior of the fibers in acetone and ethanol is different from that in benzene and THF. During the immersion in polar solvents, the main chain of the gels and the soluble components still keep its PCS struc-

ture. Both the gel and the soluble component yield almost the same quantity of inorganic silicon carbide after the pyrolysis, while oxidation curing influenced the polarity of the precursor.

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