JOURNAL OF MATERIALS SCIENCE **35** (2000) 1535–1540

Synthesis of amorphous carbon fiber from a new organosilicon precursor

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Synthesis of amorphous carbon fiber with atomic scale dispersed silicon was investigated. An organosilicon precursor (MSP), which was developed as heat resistant plastics in recent years, was used as a precursor. Temperature control during the melt-spinning was important in order to tailor precursor fibers having thin diameters. For the fiber curing, γ-ray irradiation previous to pyrolysis in an O_2 atmosphere was available. The effect of irradiation on the MSP fiber was investigated with mass change, FT-IR and SEM observation after pyrolysis. During the irradiation, oxygen was introduced in the fiber in proportion to the total dose, but the irradiation curing formed microscopic defects on the fiber surfaces at the same time which limited the resultant fiber strength. *© 2000 Kluwer Academic Publishers*

1. Introduction

In recent years, various organosilicon polymers have been systematically developed as candidates for new functional or structural materials [1–5]. The properties of the polymers containing silicon atoms is interesting from the viewpoint of the high binding energy of Si—O, Si—C, Si—N bonds and high cross-linking ability of Si—H, Si—OR, Si—Cl bonds. In these polymers, the organosilicon polymer (Commercial name: MSP) newly synthesized from phenylsilane and diethynylbenzene by dehydrogenation reaction is superior in heat resistance. This polymer forms cross-linking with heat treatments between 413 and 513 K, and shows a slight mass loss at 800–900 K. The final residual mass at 1273 K comes to be 94%, which greatly exceeds those of the foregoing structural plastics [6–9]. The appearance of the products after pyrolysis are black and glassy, which is similar to vitreous carbon synthesized from thermosetting resins, such as phenolic resin, furfurylalchol and polyimide [10, 11]. The high residual mass after pyrolysis is attractive as the precursor for new type of carbonaceous materials. Thus, we expected this polymer to be promising as the precursor of amorphous carbon fibers containing a small amount of silicon. In the synthesized fibers, silicon atoms are considered to be hybridized with carbon almost at a nano or atomic scale [1, 9, 12].

2. Experimental

A method of synthesis of a precursor polymer (MSP) was reported in foregoing articles, and the monomer unit characterized as $-Si(Ph)H-C{\equiv}C-C_6H_4-C{\equiv}C-$ [6, 13]. Mw (weight average molecular weight) and Mn (number average molecular weight) of the precursor are 5400 and 2620, respectively. The precursor was spun into fiber form by a small batch melt spinning unit built in our laboratory [14]. The precursor in the cell was maintained in vacuum during the temperature rising, and N_2 pressure slightly higher than 1 atm was applied on the precursor melt just before the spinning. The heating rate of the cell was monitored with thermocouples. The spun fibers were put into sealed glass tubes and cured with ^{60}Co γ-ray irradiation in an 1 atm pure O_2 atmosphere. The total dose used for the curing was between 0.35–6.94 MGy with a dose rate of 58.0 KGy/h. The cured fibers were subjected to IR spectra measurements using a KBr pellet method (Perkin Elmer, FT-IR 1650). The fiber pyrolysis was performed with a SiC furnace with a heating rate of 100 K/h and a holding time of 1 h at 1273 K. The morphology of the resultant fibers was investigated by scanning electron microscopy (JEOL, JSM-T20 and Hitachi, FE-SEM S-4500). The tensile strength of the resultant fibers was measured using a tesilon type testing machine (Toyo Measuring Instruments, Tensilon UTM-II) with a gauge length of 10 mm. The electrical resistivity was measured by a two-probe direct-current method (Advantest, Digital electrometer TR8652) with a gauge length of 0.8 mm. Thermogravimetric analysis was performed on 3–5 mg of a sample under a flow of air with a heating rate of 5 K/min (Rigaku, TG-8110). The X-ray diffraction was measured for the sample heat-treated in a graphite furnace on an X-ray spectrometer (Rigaku, RINT-5000).

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3. Results and discussion

In order to obtain thin fibers from MSP, temperature control during the spinning process is essential, because the polymer has a thermosetting character. MSP is known to form cross-linking by heat treatments beyond 413 K even in vacuum [6–9], but the polymer shows fluidity and strong spinability just under the cross-linking temperature.

Fig. 1 shows the diameter of the polymer fibers spun by our apparatus. The fibers having stable diameter are obtained between 393 and 413 K. Below 393 K, the polymer still contains a small amount of a non-melt yellow powder. Beyond 413 K, the viscosity of the polymer melt increases suddenly, and the melt is finally solidified. When the heating rate of the cell was decreased into 5 K/min, larger size of a orifice and higher Ar pressure was necessary to extrude the polymer melt. The resultant diameter in this case was increased into 25–30 μm. This should be due to the slight cross-linking formation between MSP chains even below 413 K. In the following experiments, the fibers spun at 403 K with a heating rate of 10 K/min are used as a standard sample.

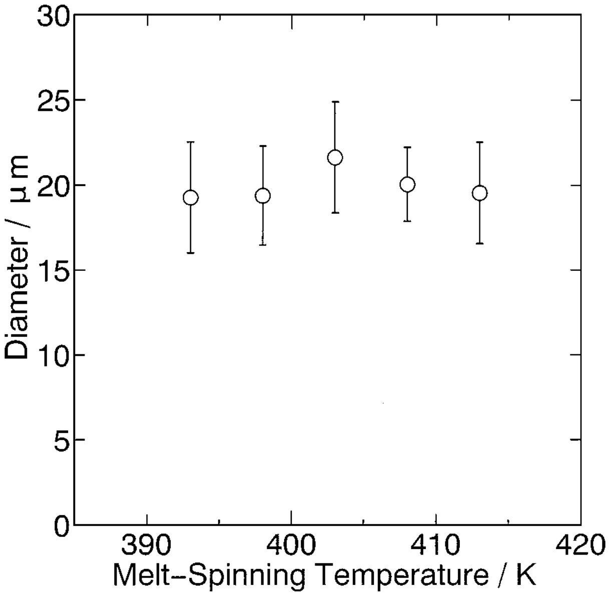


Figure 1 Diameters of melt-spun MSP fibers. (Diameter of an orifice: 1.5 mm).

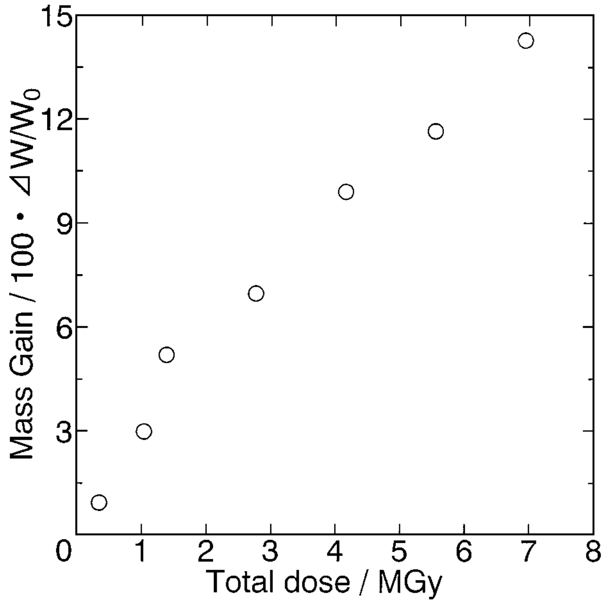


Figure 2 Mass gain of MSP fibers after irradiation curing. (Dose rate: 58.0 KGy/h, atmosphere: 1 atm O_2).

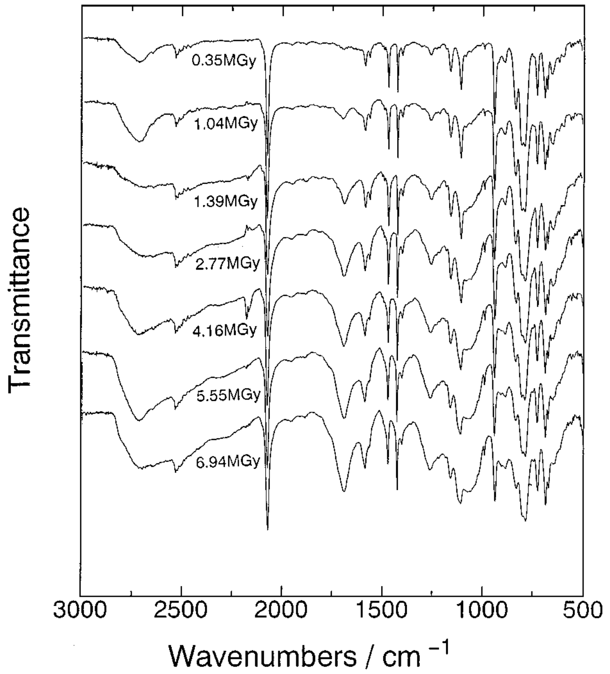


Figure 3 IR spectra of MSP fibers after the irradiation curing.

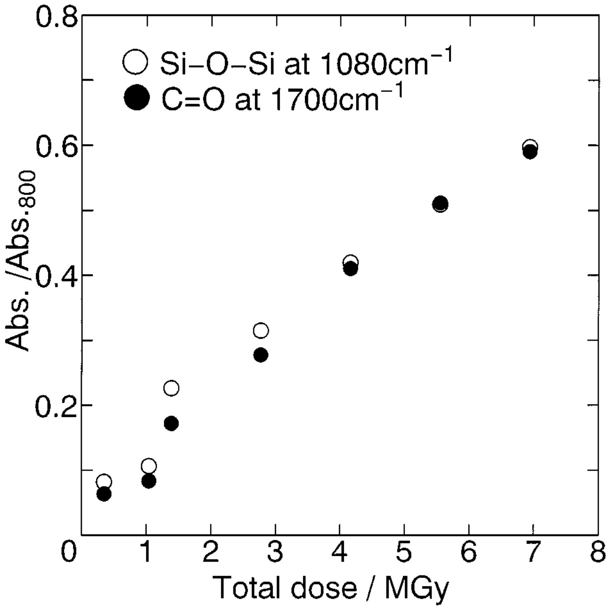


Figure 4 Relative intensity of Si—O—Si (or Si—O—C) and C═O absorption peaks after the irradiation curing. (Absorbance at 800 cm^{-1} is used as a standard).

Curing process on the fibers before pyrolysis is important to obtain shape stable ceramic fiber by the precursor method [15–17]. In the case of MSP, the polymer must be sufficiently cross-linked below 393 K which is a softening temperature of MSP. We have tested the gradual heat treatments in an O_2 gas flow and the exposition for ozone on the MSP fibers. These methods can introduce the oxygen in the polymer fibers, but are not successful in production of shape stable fibers after pyrolysis. Thus we adopted γ-ray

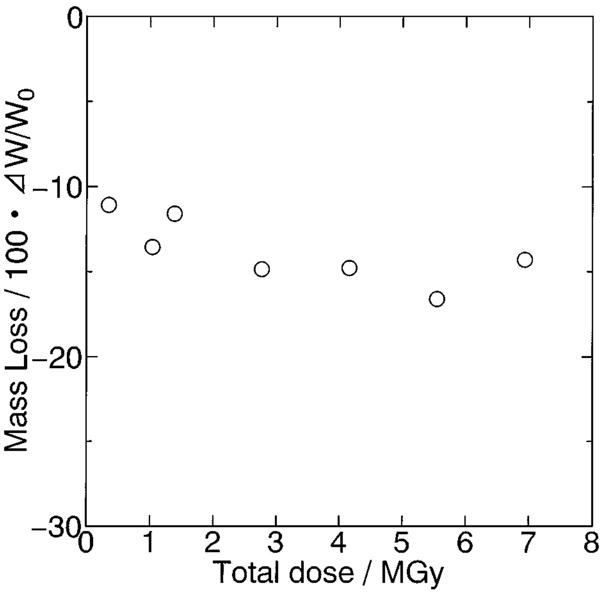


Figure 5 Mass loss of the cured MSP fibers after pyrolysis at 1273 K.

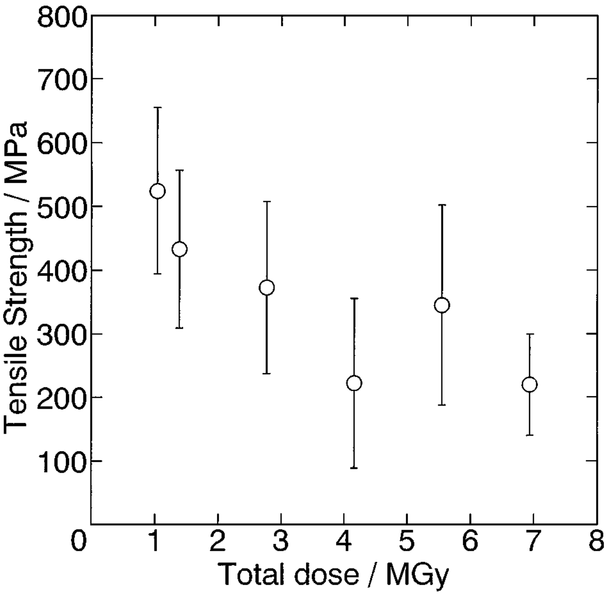
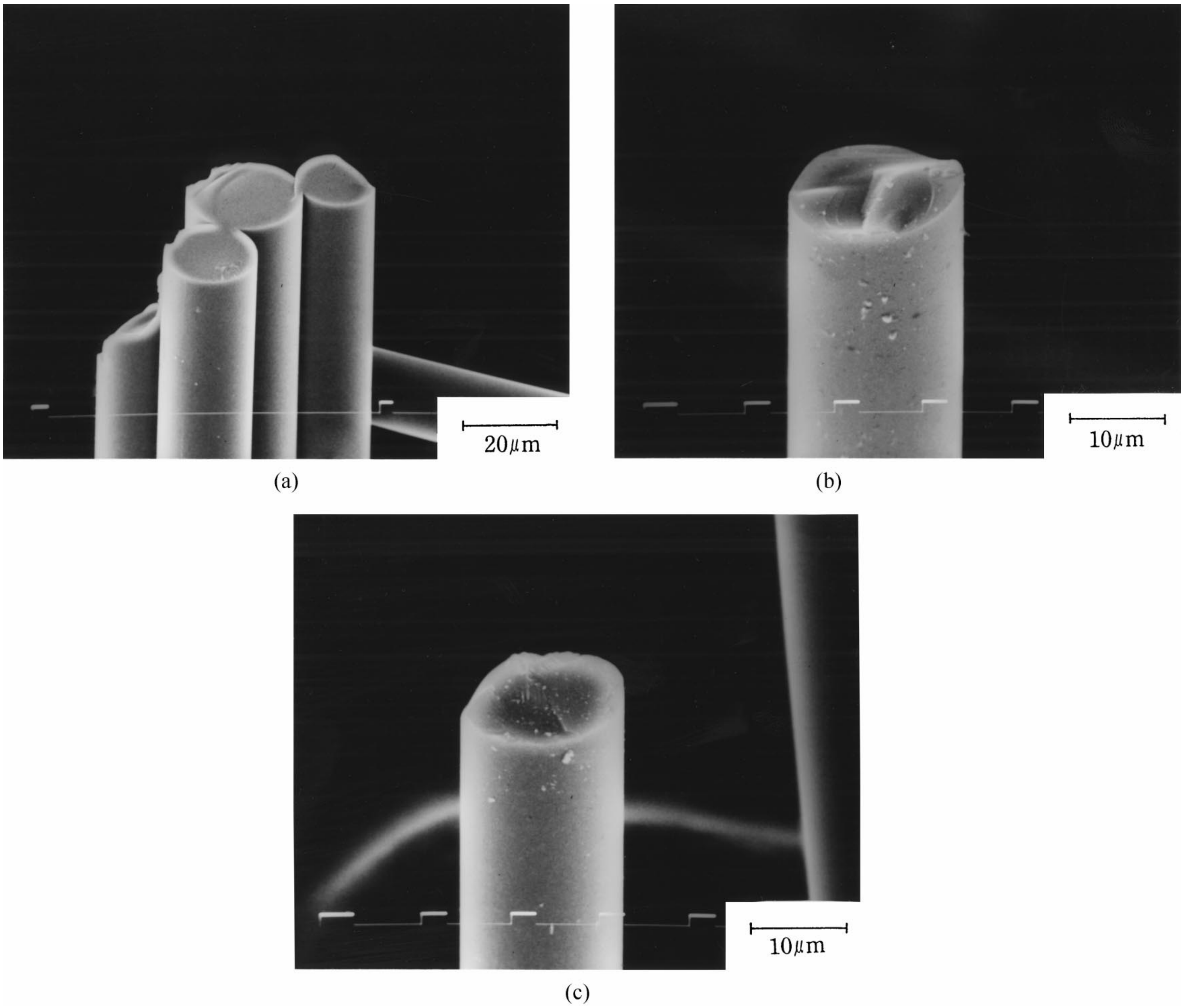


Figure 7 Tensile strength of the synthesized inorganic fibers.

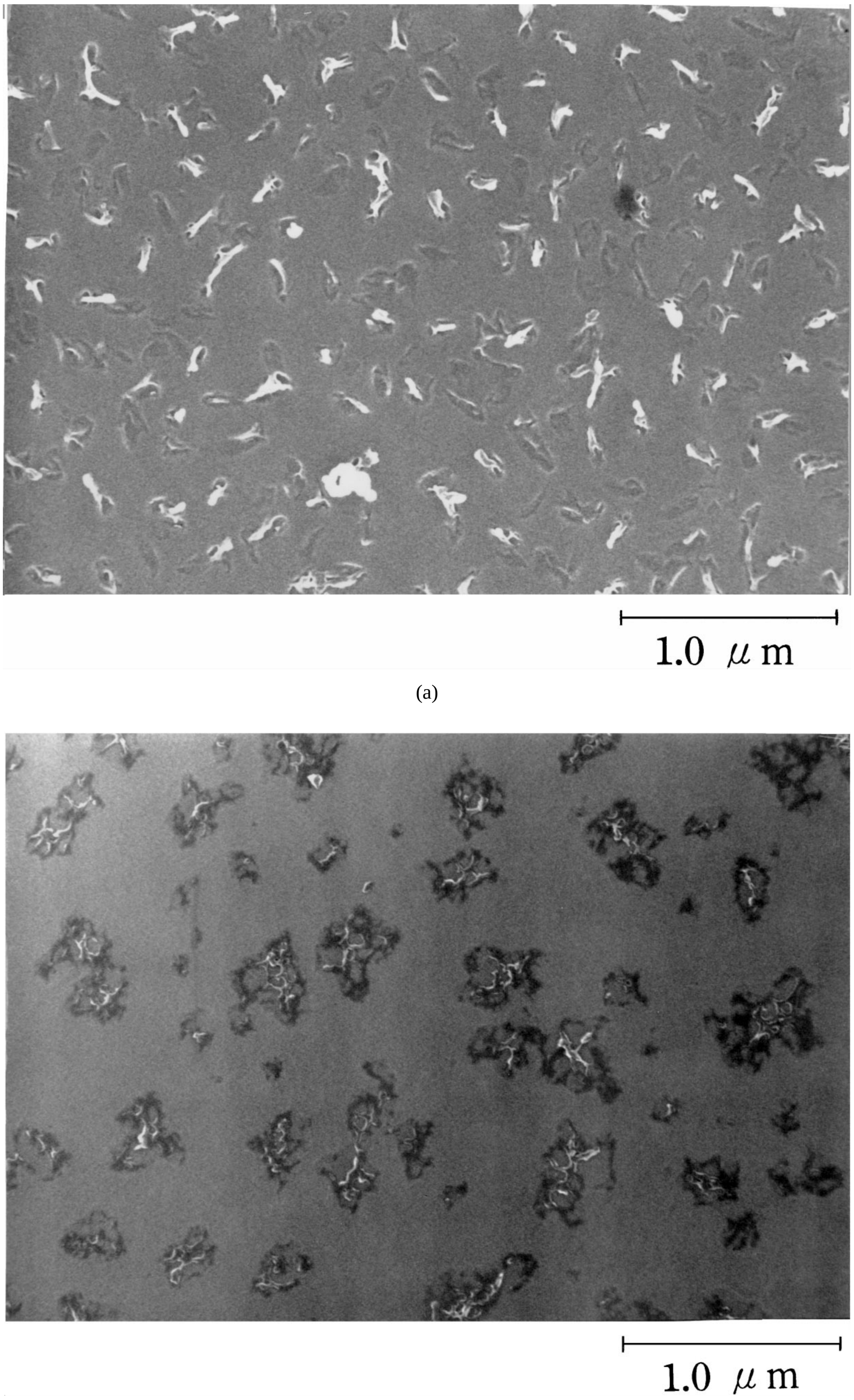


(a)

(b)

(c)

Figure 6 Cross sectional observation of MSP fibers after pyrolysis at 1273 K. (a) Cured with 0.35 MGy irradiation; (b) cured with 1.04 MGy irradiation; (c) cured with 6.94 MGy irradiation.



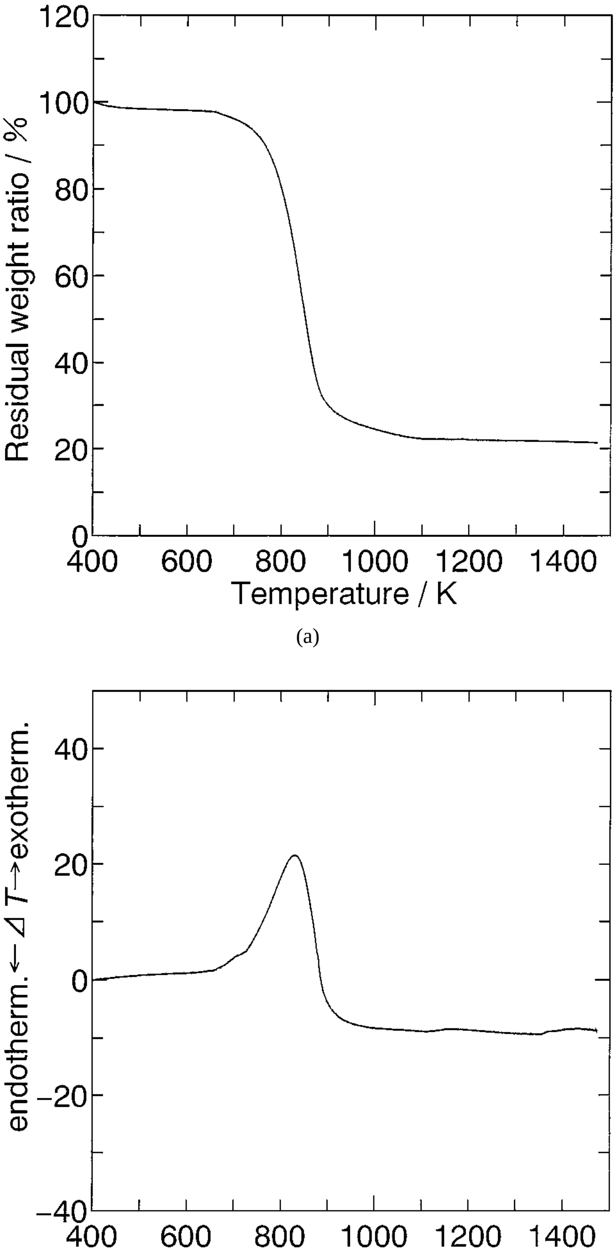
(a)

(b)

Figure 8 FE-SEM photographs of synthesized inorganic fiber surfaces. (a) Cured with 1.04 MGy irradiation; (b) cured with 6.94 MGy irradiation.

irradiation on the MSP fiber in an O_2 atmosphere, which is industrially available at present to synthesize high heat resistant SiC fibers from polycarbosilane [18, 19].

Fig. 2 shows mass gain of the polymer fiber after γ-ray irradiation. The relationship between total dose and mass gain is almost linear. 1 MGy of irradiation approximately corresponds to 2–3% of the fiber mass gain. The color of the fiber is changed from yellow into light brown after 6.94 MGy of irradiation, which would be related to the increase in conjugate double bonds in MSP. Fig. 3 shows IR spectra of the fibers after the γ-ray irradiation. As the total dose of the irradiation increases, Si—O—Si (or Si—O—C) band at 1080 cm^{-1} and C═O bands at 1700 cm^{-1} become apparent which are absent in MSP before the curing. In Fig. 4, relative intensity of Si—O—Si (or Si—O—C) and C═O absorption peak was plotted against the total dose. The intensity of the peak increases linearly with the γ-ray irradiation. FT-IR method can not determine absolute ratio of Si—O—Si (Si—O—C) groups to C═O groups in the cured fibers, but makes it clear that the formation rates of both species with the irradiation are almost equal. The change in 2100 cm^{-1} absorption peak which has been assigned to hydrosilane or



(a)

(b)

Figure 9 TG-DTA curves of the inorganic fiber in an air flow with a heating rate of 5 K/min. (Cured with 1.04 MGy irradiation). (a) TG curve; (b) DTA curve.

diacetylene groups was hardly observed, although the Si—O—Si (or Si—O—C) groups were formed during the irradiation.

During the pyrolysis, the main mass loss in MSP generally occurs at 800–900 K which originates from the elimination of small amount of phenyl groups. Fig. 5 indicates the mass loss of the fibers after the pyrolysis at 1273 K. The mass loss is always beyond 10%, and seems to be slightly decreased with the long time irradiation. 10% mass loss is somewhat larger than that of reported MSP without the irradiation. The C=O bonds formation with the irradiation may attribute such high mass loss.

SEM photographs of the synthesized inorganic fibers are shown in Fig. 6. The fiber cured with 0.35 MGy irradiation is slightly fused during the pyrolysis. The total dose beyond 1.04 MGy is necessary to achieve a sufficient curing in an 1 atm O_2 atmosphere. Tensile strength of the fiber with the 1.04 MGy irradiation is, however, 550 MPa, and that of the fiber with 6.94 MGy irradiation is 250 MPa (Fig. 7). Decrease in fiber strength is strongly concerned with the total dose, while the fiber mass loss after pyrolysis shows slight dependence on the total dose. In Fig. 8, the FE-SEM photographs of the resultant fiber surfaces at high magnification are shown. In the fiber cured with 1.04 MGy irradiation, formation of many ellipsoidal dimples in size of 100–150 nm are observed. With the 6.94 MGy irradiation, the irregular shape craters in size of 200–300 nm are observed. Almost same defects were observed on the fibers pyrolyzed at 1073 K. These defects would be irradiation damages introduced with the curing processes and reduce the intrinsic fiber strength. For tailoring the inorganic fiber from MSP, total dose must be minimized as much as the dose needed for the curing. Electrical resistivity of the fibers pyrolyzed at 1273 K are between $10^{-3} - 10^{-3.5}\ \Omega \cdot \mathrm{m}$ independent of the curing conditions. TG-DTA curves of the synthesized fiber in air are indicated in Fig. 9, main mass loss with a exothermic reaction occurs at 700–800 K which corresponds to the carbon burning. After the carbon burning, about 20% of white silica remains in the crucible. This fibrous silica should be porous, but the surface and the cross section

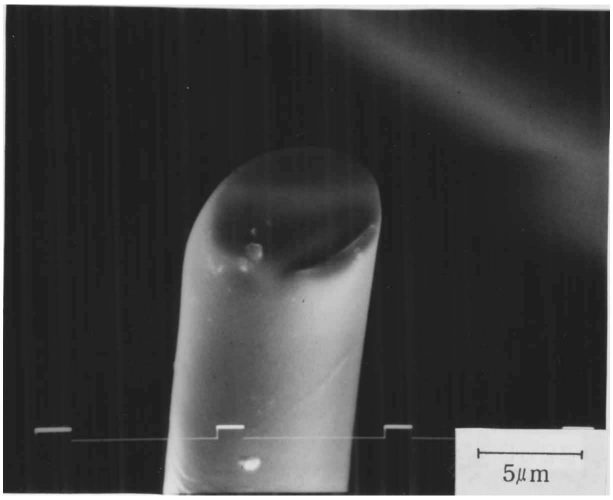


Figure 10 SEM photograph of the silica residue after carbon burning.

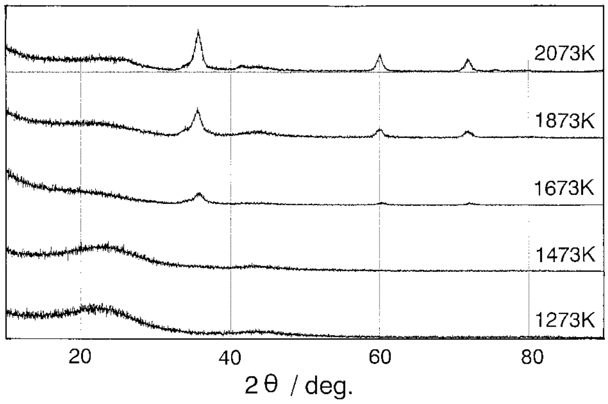


Figure 11 X-ray diffraction patterns of the synthesized inorganic fibers after heat treatments. (40 KV and 20 mA, Cu $K_{\alpha 1}$ radiation).

appear to be smooth (Fig. 10). Such homogeneous appearance probably indicates the uniform dispersion of silicon atoms into environmental carbon matrix.

The structure of the resultant fiber from MSP is amorphous up to 1473 K. The peaks of silicon carbide, however, appear in the X-ray diffraction patterns beyond 1673 K (Fig. 11). The fibers after heat treatments beyond 1673 K kept their fibrous shape, but the tensile strength decreased. The strength of the fibers after 1873 K heat treatment was about 180 MPa, and the electrical resistivity was $10^{-4}\Omega \cdot \mathrm{m}$.

4. Conclusions

Amorphous carbon fiber containing a small amount of silicon in microscopic scale is synthesized from a new organosilicon precursor (MSP). MSP can be shaped into thin fiber form by melting the precursor rapidly in vacuum beyond 393 K and with the simultaneous melt-spinning. γ-ray irradiation in an O_2 atmosphere is effective to maintain the fiber shape during the pyrolysis, but introduces 100–300 nm size of irradiation damages on the fiber surfaces which affects the fiber strength. During the irradiation curings, the oxygen is captured with the MSP fiber in the form of $\mathrm{Si{-}O{-}Si}$ (or $\mathrm{Si{-}O{-}C}$) and $\mathrm{C{=}O}$ groups linearly dependent on the total dose. After the pyrolysis at 1273 K, the fiber is amorphous, but SiC microcrystals begin to precipitate with a heating beyond 1673 K.

Acknowledgement

We thank Professor T. Dohmaru in Research Institute for Advanced Science and Technology in Osaka Prefecture University for kind advice about the γ-ray irradiation of the sample fiber in the closed tube cells. We thank Mr. T. Kawano in Research Institute for Advanced Science and Technology in Osaka Prefecture University for help in preparing the tube cells for the irradiation. We thank Dr. M. Sugimoto and Dr. T. Seguchi in Takasaki Radiation Chemistry Research Establishment in Japan Atomic Energy Institute for advice about the γ-ray irradiation effect on organosilicon polymers.

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Received 11 July 1997
and accepted 30 September 1999