Melt Spinning and Metal Chloride Vapor Curing Process on Polymethylsilsesquioxane as Si—O—C Fiber Precursor

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ABSTRACT: Melt spinning process of polymethylsilsesquioxane (PMSQ) at 403–453 K was investigated as a Si—O—C fiber precursor in terms of averages and distributions of spun fiber diameters. Because of fusible character of PMSQ at low temperature, the spun fibers were exposed to vapors of various metal chlorides (SiCl$_4$, Si(CH$_3$)Cl$_3$, TiCl$_4$, and BCl$_3$) to promote the fiber curing. Cured fibers were investigated by FTIR and TG analyses. In a case of the fiber synthesized with SiCl$_4$ curing, tensile tests on the pyrolyzed fibers were performed. Exposure of the synthesized fiber at high temperature with a flame of an oxygen-gas burner was examined. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2600–2607, 2009

Key words: crosslinking; fibers; nanocomposites; silicones; thermosets

INTRODUCTION

Ceramic fibers, including carbon, glass, alumina, and silicon carbide fiber, are key materials in modern industry as reinforcements of various composites. In particular, flexible continuous SiC base fibers synthesized by precursor methods show extremely high heat resistance even in an oxidation atmosphere and they are mainly used as reinforcements in ceramic matrix composites in recent years.[1–3] Starting polymer for the SiC base fibers, polycarbosilane (PCS), is, however, synthesized with multistep process, including dechlorination reaction of dimethyldichlorosilane with sodium, precipitation of resulting polydimethylsilane (PDMS) from solvent, and thermal condensation reaction of PDMS to PCS at 673 K. Fractionation of the resulting PCS by molecular weight is also necessary.[2,4–6] In addition, the recent advanced SiC base fiber synthesis often requires noble chemical techniques, such as radiation curing, pyrolysis in a hydrogen-rich atmosphere, or addition of sintering aids in starting PCS.[7–10] These procedures tend to increase production costs of the resulting SiC base fibers.

On the other hand, Si—C—O materials derived from PCS with thermal oxidation curing and Si—O—C materials derived from silicone resin or silicon alkoxide have been studied as ceramic precursor for long years. Thermal oxidation treatment on PCS is a simple process, and relatively low modulus of resulting Si—C—O fibers with high tensile strength is appropriate for fabricating reinforcement fibers in 2D or 3D fabrics.[4,5] On the other hand, Si—O—C materials are attractive because of precise control of starting molecular structure. Modification of chemical composition is available in various stages from synthesis, crosslinking, and ceramization steps.[11–16]

Heat resistance of such Si—O—C or Si—C—O materials is, however, limited when compared with pure SiC or Si-exC materials because of CO and SiO evolution at high temperature [eq. (1)].

$$\text{Si—C—O or Si—O—C} \rightarrow \text{SiC} + \alpha\text{CO} + \beta\text{SiO} + (\gamma\text{C}) \tag{1}$$
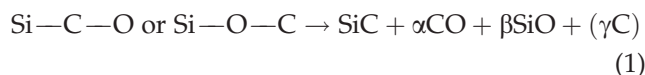
This reaction is known to start at 1473–1673 K in an inert atmosphere.[17,18] This is a limit of heat resistance of Si—C—O or Si—O—C.

On the other hand, it is reported that the Si—O—C material shows available oxidation resistance at 1473 K, which depend on carbon content, residual Si—C bond, and ability of protective silica layer formation on material surface.[19] Therefore, we expect that the ceramic fiber with Si—O—C chemical composition (with a low C content) is promising for conventional

industrial materials with middle class heat resistance as well as Si—C—O fibers.

As the starting precursor must satisfy an intrinsic low cost factor, we paid attention to polymethylsilsesquioxane (PMSQ). PMSQ is synthesized from trichloromethylsilane, which is a major subproduct in classic Rochow process.[20] As dimethyldichrosilane is an indispensable monomer in silicone industry, methyltrichlorosilane is also obtained in mass scale. It means that intrinsic cost of PMSQ is far lower than that of organometallic monomers or polymers synthesized by noble chemical techniques.

In this study, we indicate cermization data of PMSQ at first, because various kinds of silicone resins called PMSQ are now commercially available. Melt spinning process of PMSQ is investigated as a function of spinning temperature and a holding time. To solve a problem of PMSQ fusibility, metal chloride vapor curing was adopted on spun PMSQ fibers.[21] Costs of original PMSQ and metal chloride are low. Therefore, Si—O—C fiber synthesized by this method is expected to be used in a field of a fundamental industry as a heat insulator, a heat resistant DPF filter, and a catalyst support in a high-temperature chemical plant.

EXPERIMENTAL SECTION

Polymethylsilsesquioxane (YR 3370, Momentive Performance Materials, Tokyo, Japan) in a form of a transparent solid was used after characterization. The polymer was melt spun to fiber form by using melt spinning unit built in our laboratory.[22] Important dimensions of a spinning glass tube are shown in Figure 1. The spinning temperature was controlled at 403, 423, or 453 K. The diameter of the spun fiber was measured by BS-D8000 Digital Microscope (SONIC, Osaka, Japan). For the curing process, $SiCl_4$ (Tokyo Chemical Industry, Tokyo, Japan), CH_3SiCl_3 (Tokyo Chemical Industry), $TiCl_4$ (Wako Pure Chemical Industries, Osaka, Japan), and $1.0M$ BCl_3 in *para*-xylene solution (Sigma-Aldrich Japan, Tokyo, Japan) were prepared. The spun fibers were put in an enamel bat with a capacity of 800 cm^3. Ten milliliters of a curing agent in a Teflon dish was also placed in the same enamel bat. The bat was covered by a large glass plate, and the system was usually held for 1 h to achieve saturation of a metal chloride vapor. All the procedures were performed in a glove bag with a flow of nitrogen gas (2 L/min) to avoid influence of moisture or oxygen. Besides the room temperature (ca. 299 K), the bat was heated at 309 K to increase the vapor pressure of the curing agent. FTIR spectra of as-spun fiber and cured fibers were obtained by Spectrum GX (Perkin Elmer Japan, Yokohama, Japan). TG analysis was performed by TAS-100 (Rigaku, Tokyo, Japan) with a flow of Ar gas. At high-temperature region in an inert atmosphere, a TG curve was meas-
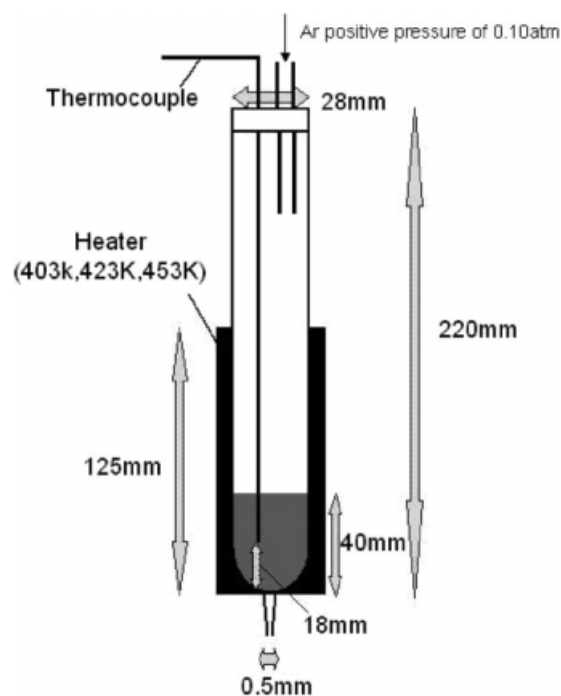

Figure 1 Important dimensions of a glass tube and heating elements used for melt spinning.

ured by self-made system, equipped with a vertical furnace of $MoSi_2$ heaters. The cured fibers were pyrolyzed at 1273 K in an Ar atmosphere with a heating rate of 200 K/h with a holding time of 1 h. Oxidation resistance of resulting fiber was investigated by TG analysis with a flow of air up to 1673 K. For preliminary heat resistant tests, the obtained fibers were exposed to a blue flame burner. Temperature in a flame environment was estimated to be 1673–1723 K by a portable radiation thermometer (CHINO IR-AH). The morphologies of the pyrolyzed fibers were observed by FE-SEM, S-4500 (Hitachi). The tensile strength of the pyrolyzed fiber was measured using a Tensilion UTM-II (Toyo Measuring Instruments) with a gauge length of 10 mm and a crosshead speed of 2 mm/min. Measurements were carried out 20 times on one sample and results were averaged.

RESULTS AND DISCUSSION

Ceramization process of PMSQ

First synthesis process of PMSQ, which was soluble for organic solvents, was reported in 1978.[23] Until now, various kinds of PMSQ with different molecular structure have been synthesized.[24] Because chemical and physical characters of the starting PMSQ depend on synthesis method, we describe detailed ceramization data of the PMSQ used in this study before fiber synthesis.

Figure 2 shows a TG curve of PMSQ powder in an Ar gas flow. A curve up to 1273 K was obtained
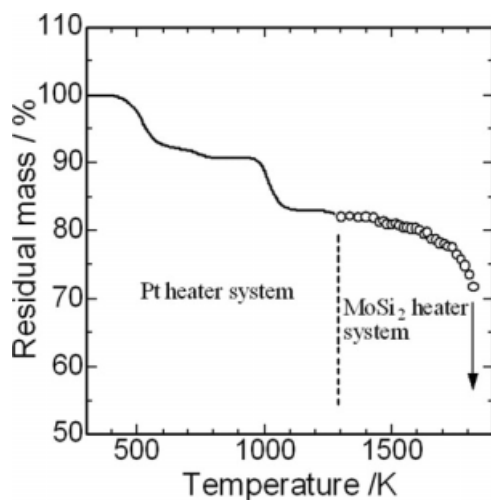
Figure 2 Convoluted TG curve of balk PMSQ in an Ar gas flow (heating rate up to 1273 K was 10 K/min, and that beyond 1273 K was 3.3 K/min).

by TAS-100 for 10 mg of sample with an alumina crucible in an Ar gas flow. A curve beyond 1273 K was obtained for 1 g of sample by an automatic balance equipped with a vertical $MoSi_2$ furnace with a graphite crucible in an Ar gas flow. Therefore, the curve in Figure 2 was a convolution of two data.

The results of spectroscopic analysis on pyrolyzed PMSQ were reported in a previous study.[25,29] Si NMR spectrum of starting PMSQ indicated a signal of T ($SiCO_3$) environment at -65 ppm. Existence of silanol groups was suggested by a signal of T^2 ($CSi(OSi)_2(OH)$) at -59 ppm. After crosslinking with heat treatment at 573 K, the signal assigned to T^2 disappeared and the signal of T became dominant. Ceramization of PMSQ proceeded at 1073 K, which corresponded to broadening of the T signal and appearance of new signals of M (SiC_3O) at 7 ppm, D (SiC_2O_2) at -21 ppm, and Q (SiO_4) at -107 ppm.

Thus, the mass loss at 473–573 K is assigned to crosslinking of silanol groups with evolution of H_2O. The second mass loss at 973–1073 K is assigned to ceramization process with evolution of methane. At a temperature range of 1073–1673 K, there is no apparent mass loss in a TG curve. XRD patterns of heat-treated samples at 1273 or 1673 K are shown in Figure 3. Chemical composition of Si—O—C material pyrolyzed at 1673 K was evaluated to be $SiC_{1.5}O_{0.68}$ by an elemental analysis (KOBELCO Research Institute). The sample pyrolyzed at 1273 K may contain a small amount of hydrogen. The Si, O, and C molar ratios are, however, probably stable at 1073–1673 K. The sample heated at 1273 K shows only broad lines at 22° and 68°, which are assigned to amorphous silica. After 1673 K heat treatment, however, broad lines at 35°, 60°, and 72° appear. These lines are assigned to β-SiC with a small crystallite size. The

mass loss beyond 1673 K is assigned to evolution of SiO and CO from Si—C—O or Si—O—C amorphous state in general. Because the graphite crucible was used for a high-temperature TG measurement, a part of the mass loss may be caused by indirect reactions between the Si—O—C amorphous and graphite. During the holding at maximum temperature at 1833 K, the mass loss does not finish and continues monotonously.

Continuous melt spinning of PMSQ was successful at 403–453 K in a spinning speed of 10 m/s. Figure 4(a–c) shows distributions of spun fiber diameters obtained at each temperature. The diameter of the spun fibers strongly depends on the spinning temperature. The averages of the fiber diameters are 30.0 ± 7.1, 25.4 ± 4.2, and 51.7 ± 6.4 μm for 403, 423, and 453 K, respectively.[21] The most suitable temperature to obtain thin fiber is 423 K. The average diameter of the spun fiber is, however, larger than that of PCS fiber (19.4 μm) obtained by the same spinning unit. It reveals that the viscosity of PMSQ melt was always higher than that of PCS melt. This tendency possibly corresponds to thermosetting nature of PMSQ reported by Wang et al.[26] They observed increase in PMSQ viscosity at 393–403 K with a holding time beyond 300 s. The wide distribution in diameter observed at 453 K also suggests influence of melt hardening with partial crosslinking of PMSQ molecules. Even at 423 K, such partial crosslinking may increase the melt viscosity. To diminish the influence of the melt hardening, the holding time at 423 K was shortened. Figure 4(d) shows resulting fiber diameters spun with a holding time of 20 min at 423 K. The average diameter decreased to 16.8 ± 1.4 μm, which is 66% of the average diameter obtained after 60 min holding time. Adjusting of temperature and holding time was necessary to produce thin PMSQ fibers.

Ordinary thermal oxidation curing was tried on spun PMSQ fiber with a heating rate of 40 K/min up to 453 K. During the oxidation process, however,
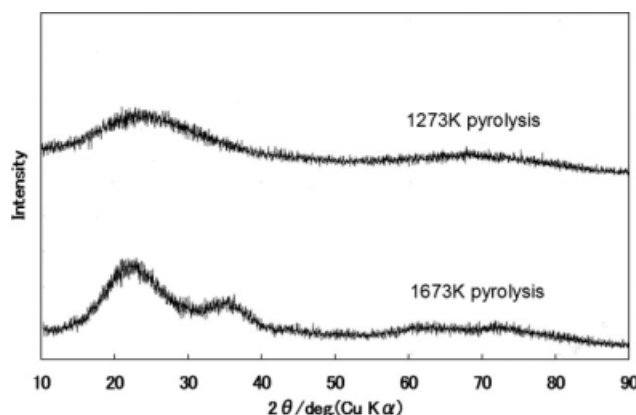

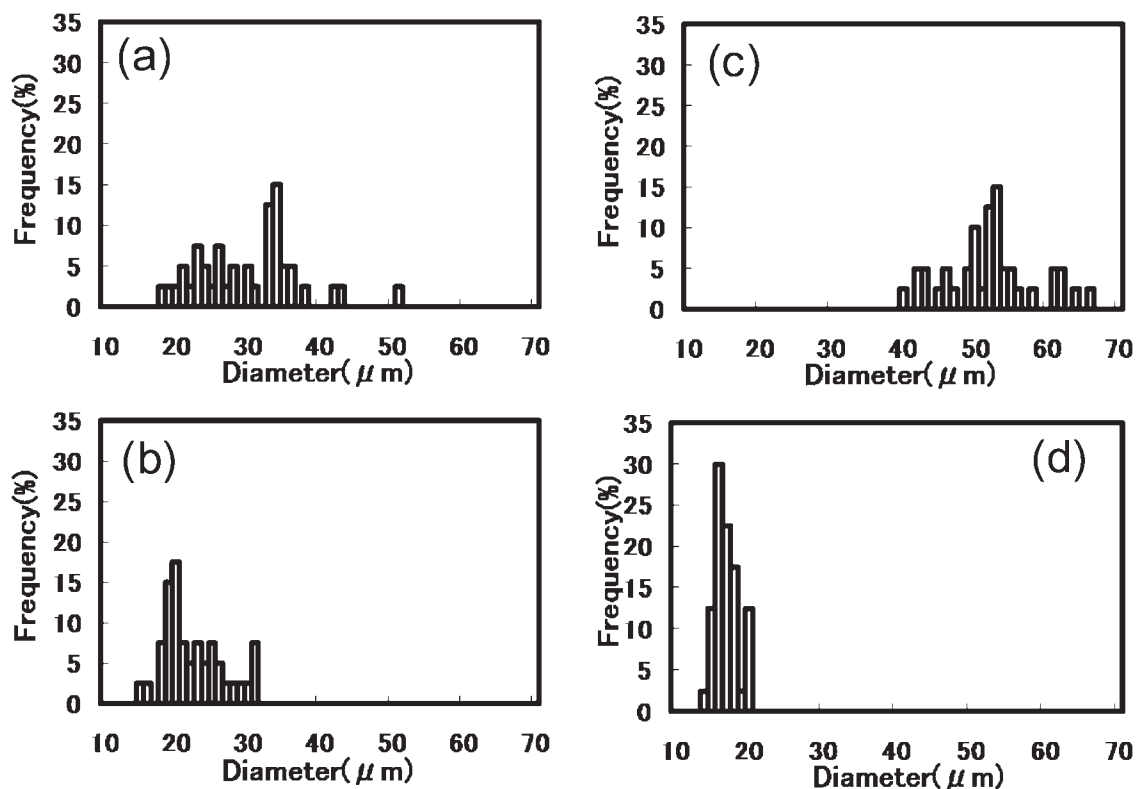**Figure 3** XRD patterns of pyrolyzed PMSQ materials.

Figure 4 Diameter distributions of PMSQ fibers spun at various temperatures: (a) 403 K with 60 min holding, (b) 423 K with 60 min holding, (c) 453 K with 60 min holding, and (d) 423 K with 20 min holding.

the spun fiber was completely melted down. It was easily expectable from intrinsic melt spinning temperature of PMSQ. To cure the spun fiber below softening temperature, the spun fiber was exposed to vapor of metal chlorides in an inert atmosphere, and the exposed fibers were pyrolyzed at 1273 K. Some kinds of metal chloride are known to be effective to crosslink ceramic precursor polymers with modification of their starting chemical compositions.[27] In the case of ceramic fibers, $HSiCl_3$ has been used as a curing agent in the synthesis process of $SiBN_3C$ fibers.[28] Detail of the curing mechanism in this case was, however, not described.

The calculated vapor pressures of $SiCl_4$, CH_3SiCl_3, $TiCl_4$, and 1.0 M BCl_3 in *para*-xylene solution were 3.28×10^4, 2.35×10^4, 1.43×10^3, and 1.00×10^4 Pa at room temperature (299 K) and 4.67×10^4, 3.40×10^4, 2.25×10^3, and 1.40×10^4 Pa, respectively, at 308 K. These vapor pressures were calculated from Antoine equations.[29–31] After curing and pyrolysis at 1273 K, the fiber bundles were glanced by optics (Table I). $SiCl_4$ was effective to hold fiber shape after pyrolysis. Curing process by $TiCl_4$ required higher heat treatment temperature, 308 K, possibly because of relatively low vapor pressure of $TiCl_4$. BCl_3–xylene solution was effective to hold the bundle shape. Fusing between monofilaments was, however, remarkable. CH_3SiCl_3 was not effective as a curing

agent in spite of expected high vapor pressures. The bundles exposed to CH_3SiCl_3 have been melted down during pyrolysis. Mass gains after curing were about 2% for $SiCl_4$ (room temperature), 24% for $TiCl_4$ (308K), and 5% for BCl_3 (room temperature).

Figure 5 shows TG curves of the cured fibers in an inert atmosphere. After the curing process, first mass loss at 473–573 K assigned to H_2O evolution is substantially reduced and the resulting ceramic yield increases. The residual mass at 1273 K of the individual cured fiber is 92, 88, or 89% for $SiCl_4$, $TiCl_4$, or BCl_3, respectively. All the fiber can acquire higher ceramic yield after metal chloride vapor curing. Small mass losses observed in the $TiCl_4$-cured or

TABLE I
Effect of Metal Chloride Vapor Curing on PMSQ Fibers

	Room temperature (299 K)	308 K
$SiCl_4$	○	○
CH_3SiCl_3	×	×
$TiCl_4$	×	△
1.0M BCl_3 in *p*-xylene solution	△ ×	△ ×

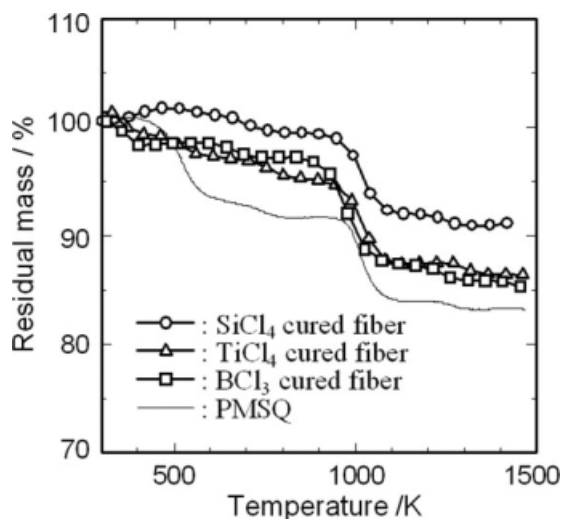○, Tensile test was possible; △, holding fibrous shape; ×, melt down during pyrolysis.

Figure 5 TG curves of cured PMSQ fibers in an Ar gas flow with a heating rate of 10 K/min.

BCl$_3$-cured fibers up to 473 K in the TG curves may correspond to the decomposition of Ti—Cl or B—Cl bonds remained in the fiber.

Figure 6 shows IR spectra of spun fiber, SiCl$_4$-cured fiber, and Si—O—C fiber obtained at 1273 K. The IR spectra reveal the Si—OH disappearance after the curing.

Figure 7(a–c) shows SEM images of Si—O—C fibers derived from the fiber cured with SiCl$_4$. Two kinds of fibers were prepared for SEM observation. One (Si—C—O) was thick fiber with strength of 0.19 ± 0.07 GPa. Another was thin fiber with strength of 0.30 ± 0.13 GPa. Curing of thin fibers was per-
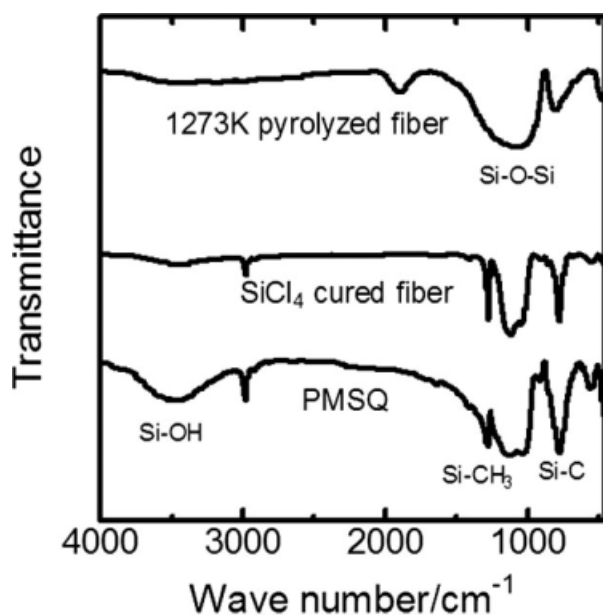

Figure 6 IR spectra of PMSQ, SiCl$_4$-cured, and 1273 K pyrolyzed fibers.
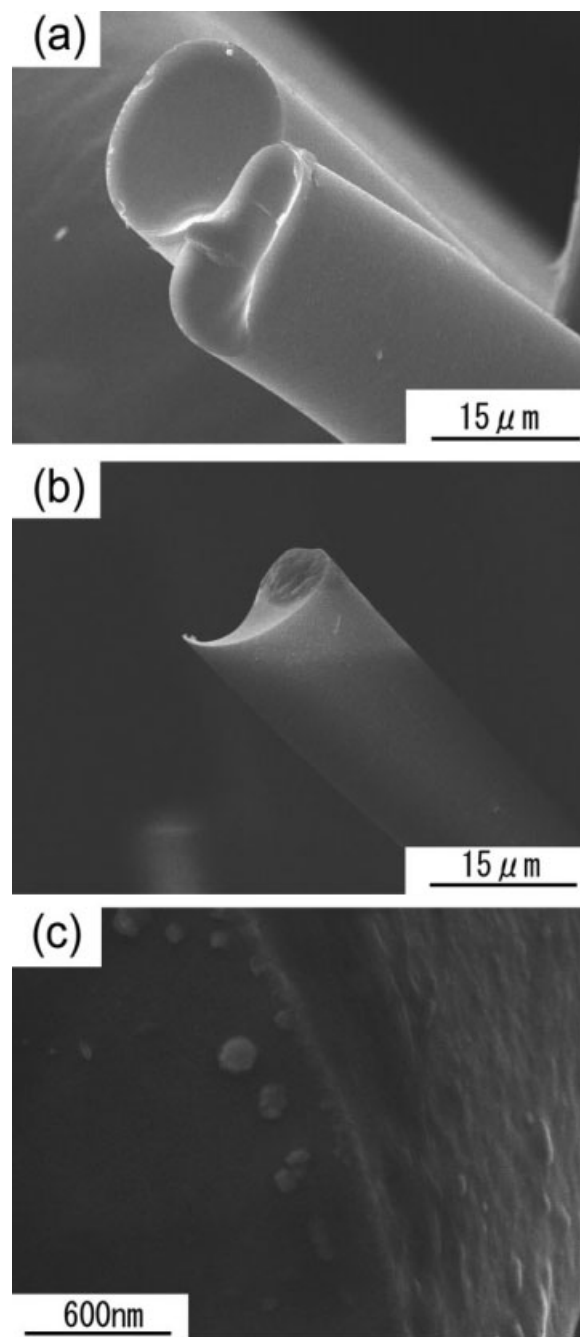
Figure 7 SEM images of Si—O—C fibers with SiCl$_4$ curing and 1273 K pyrolysis: (a) cross-section of thick fiber; (b) cross-section of thin fiber; (c) cross-section of thin fiber with high magnification.

formed at room temperature and 7 h was adopted for a curing period. Cross-section of thick fiber is smooth and indication of brittle fracture is observed. On the other hand, fracture surface of thin fiber sometimes showed microstructure, which may correspond to penetration of crosslinking agent (SiCl$_4$) in the fibers. Surface looks smooth in appearance. At high magnification, however, adhesion of small droplets is observed. It reveals that curing process
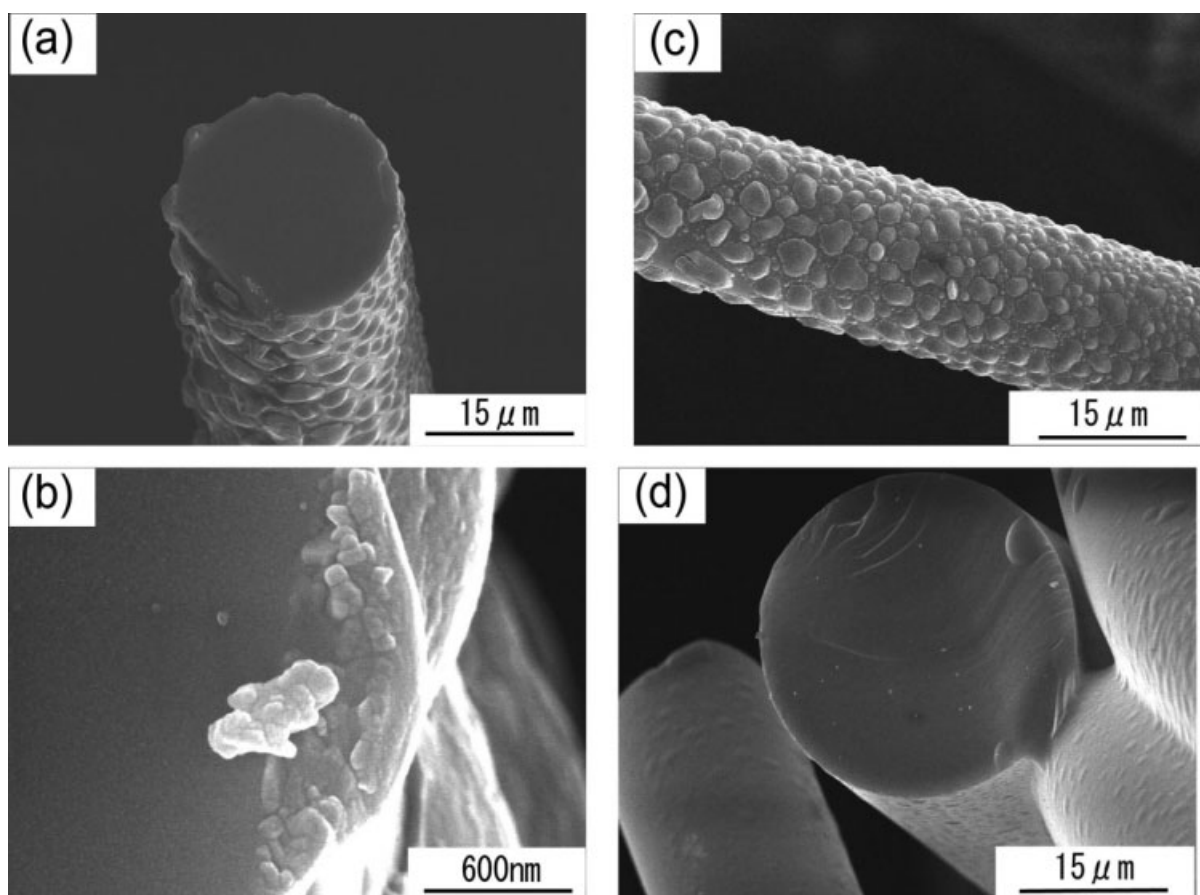
Figure 8 SEM images of Si—O—C—M fibers with TiCl$_4$ or BCl$_3$ curing and 1273 K pyrolysis: (a) cross-section of Si—O—C—Ti fiber; (b) cross-section of attached grains on Si—O—C—Ti fiber; (c) surface of Si—O—C—Ti fiber with high magnification; (d) cross-section of a fused bundle of Si—O—C—B fibers.

did not proceed completely even in the case of thin fiber with elongated curing time.

Figure 8(a–c) shows SEM images of Si—O—C—Ti fibers derived from the fiber cured with TiCl$_4$. A number of large grains adhere on the pyrolyzed fiber surface. Observation of such small grain at high magnification indicates that the grain consists of small crystals. Adhesion between grains and fiber surface looks strong. Such grains often make bridges between monofilaments. Because of such bridges, the tensile tests on monofilaments were difficult. An elemental mapping and XRD analyses of Si—O—C—Ti fiber suggested existence of TiO$_2$ (rutile and a small amount of anatase) on the fiber surface.

Figure 8(d) shows SEM images of Si—O—C—B fibers. To find independent monofilaments was almost impossible. In the case of independent mono-filament occasionally, the disk-like particles adhere on the fiber surface. This may correspond to B$_2$O$_3$ derived from boric acid during pyrolysis.

To investigate high temperature stability, TG curves of thin Si—O—C fibers (SiCl$_4$ curing) in an air flow were measured up to 1673 K (Fig. 9). The fiber is not completely stable and showed mass loss of 8%

up to 1673 K. Such mass loss is curious because the conversion reaction of the Si—O—C amorphous (chemical composition of SiO$_{1.5}$C$_{0.68}$) to silica (SiO$_2$) is expected not to cause substantial mass loss. Removal of carbon is compensated by captured oxygen in this case. The thermal decomposition of inner area of the fiber is considerable mechanism to
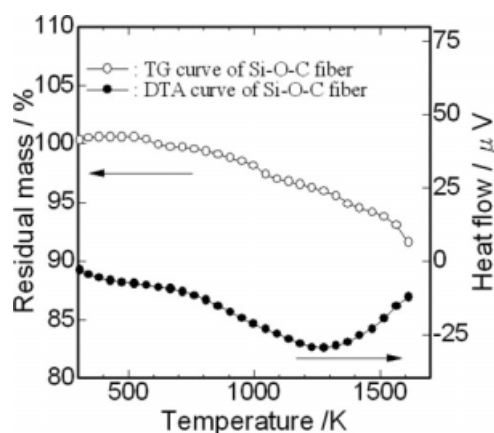

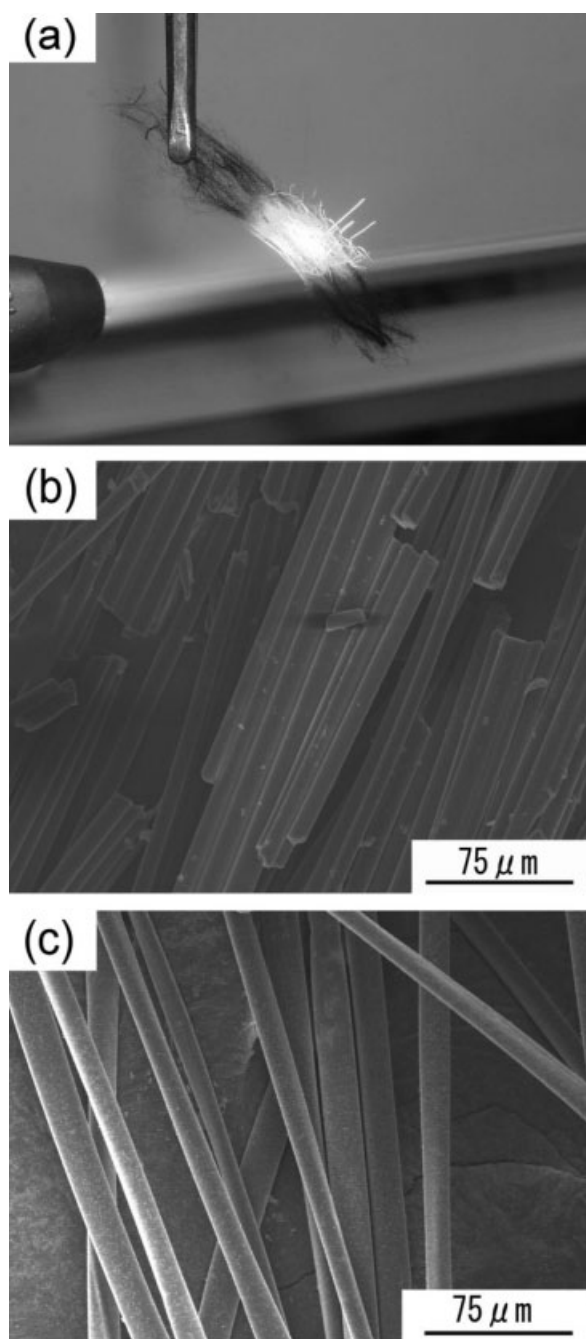**Figure 9** TG curve of Si—O—C fibers in an air flow.

Figure 10 Preliminary heat resistant test of Si—O—C fibers with gas-oxygen blue flame (1673–1734 K estimated by a radiation thermometer): (a) situation of the performed heat resistance test; (b) SEM image after 1 min exposure; (c) SEM image after 20 min exposure.

explain mass loss, while surface of the fiber was oxidized. Even after TG analysis at 1673 K, fiber holds monofilament shapes with black color. Anyway, oxidation resistant mechanism of the Si—O—C fiber needs further investigation from a viewpoint of microstructure change during the oxidation.

Figure 10(a) shows a situation of practical heat stability tests of the obtained Si—O—C fiber with

exposure to an oxygen-gas blue flame (1673–1723 K). In such situation, quartz (pure silica) fiber, which was prepared for a reference, was completely broken and melted down just after 10 s exposure.[25] Figure 10(b) shows a SEM image of Si—O—C fiber after 1 min exposure. There is no indication of fiber degradation. Figure 10(c) shows Si—O—C fiber bundle after 20 min exposure. Even after such treatment, only partial fusing between monofilaments is observed. These results absolutely indicate high thermal stability of the synthesized Si—O—C fibers when compared with quartz fibers. Existence of oxidized surface layer is difficult to be confirmed. At high magnification of the fiber cross-section, however, relatively smooth structure with 1 µm thickness from fiber surface is observed on inner rough structure (Fig. 11). This may be the silica layer formed in the Si—O—C fiber.

Starting cost of precursor for the Si—O—C fiber derived from PMSQ is far lower than that of PCS. The spinning and curing processes do not require any special equipment. The as-spun PMSQ fibers are sufficiently stable in air and moisture. This process is promising to obtain new class of conventional ceramic fibers for wide application.
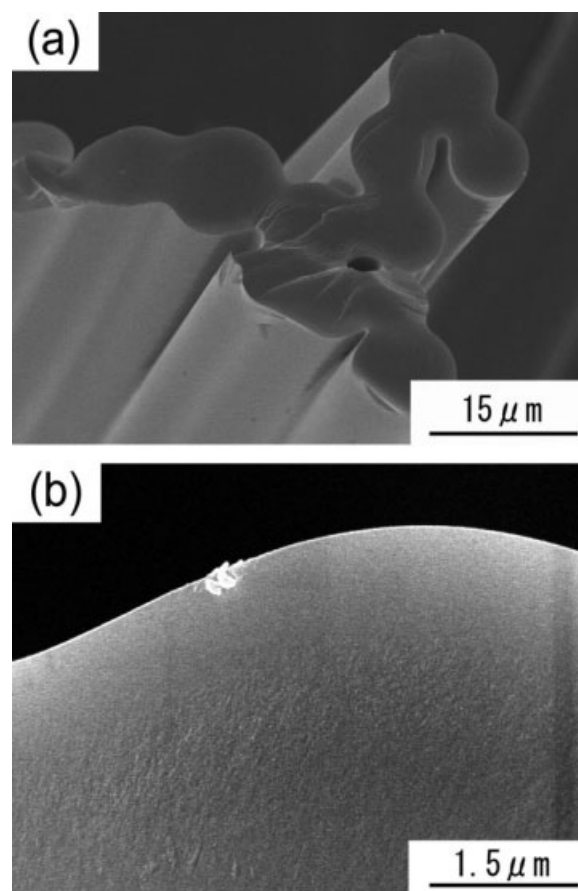

Figure 11 SEM images of Si—O—C fiber bundles after 20 min exposure: (a) SEM image of fused area; (b) SEM image of fused area with high magnification.

CONCLUSIONS

Melt spinning process of PMSQ depends on thermosetting nature of the polymer. The most suitable temperature for melt spinning is 423 K. The short holding time before spinning is also favorable. The averaged diameter of the finest PMSQ fiber is 16.8 ± 1.4 μm, which is obtained under the adjusted spinning conditions. Because of fusible character of PMSQ at low temperature, ordinary thermal oxidation curing is not available. The $SiCl_4$ vapor is effective for holding monofilament even at room temperature. In the present condition, averaged strength of 0.30 ± 0.13 GPa was obtained. The rough surface structure suggests that curing process does not proceed completely at the inner area of the treated fibers. In the case of $TiCl_4$, higher temperature (309 K) is required for holding the fiber form. The Si—O—C—Ti fiber surface using $TiCl_4$ as a curing agent strongly attaches irregular TiO_2 grains. Preliminary heat-resistant tests with an exposure of Si—O—C fiber on an oxygen-gas blue flame (1673–1723 K) reveal high heat resistance. Fiber looks stable after 1 min exposure. After the exposure for 20 min, however, fusing of fibers with forming surface silica layer is suggested.

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