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Investigation of Curing Process on Melt Spun Polymethylsilsesquioxane Fiber as Precursor for Silicon Oxycarbide Fibers

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Abstract. Polymethylsilsesquioxane (PMSQ) fiber was exposed to metal chloride vapors in a controlled atmosphere or electron beam irradiation in air to promote the curing process. The cured fibers were pyrolyzed at 1273K to compare the efficiency of individual curing method. The cured fibers were investigated by FT-IR, an optical microscope and TG analysis. In the case of successful curing, averaged diameter and tensile strength were analyzed on the obtained Si-O-C fibers.

Introduction

A number of siloxane backbone polymers (silicone resin) have been investigated as a binding agent in balk ceramic materials, matrix source of ceramic matrix composites, and starting precursors for ceramic porous bodies or coatings [1-4]. Application of such silicone resins for ceramic fiber precursor is, however, rare except the early try of Hurwitz in 1980s [1]. In general, heat resistance of Si-O-C derived from such silicone resins is believed to be far lower than that of Si-C or Si-exC. Estimation of oxidation resistance on the Si-O-C materials, however, suggested that the resistance strongly depended on carbon content and a number of Si-C bond remained in the pyrolyzed materials [5]. Reported long life time at 1473K is sufficiently promising as heat insulators and corrosion resistant filters available at high temperature. Simple chemical composition with silicon, carbon and oxygen without special elements is also attractive for industrial uses.

Since the materials utility will be limited in the conventional industry, starting precursor for Si-O-C (with low carbon content) must satisfy a factor of low cost. From such economical viewpoint, a polymer called polymethylsilsesquioxane (PMSQ) is most promising candidate for Si-O-C precursor. CH_3SiCl_3, which is a starting monomer for PMSQ, is major sub product of classic Rochow process [6]. It means that CH_3SiCl_3 is naturally supplied in a mass scale in silicone industry, and intrinsic cost of PMSQ can be reduced to quite low.

Here, we report evaluations of melt spinnability and effective curing process of PMSQ. Since the softening point of PMSQ is low, curing on the spun fiber was performed at vicinity of room temperature by using metal chloride vapor or electron beam irradiation [7,8]. Effect of the curing method on obtained Si-O-C fibers was investigated. In successful cases, tensile tests were performed on pyrolyzed fibers. Preliminary estimation of heat resistivity of Si-O-C fibers was performed by exposing the fibers on flame of a gas-oxygen burner.

Experimental

Polymethylsilsesquioxane (YR 3370, Momentive Performance Materials Japan) in a form of a transparent solid was prepared for melt spinning process. Since various PMSQ with different molecular structure (First PMSQ soluble in organic solvent was synthesized in 1978 [9,10]) is available in industry, molecular structure, ceramization process and viscoelastic properties of the used PMSQ must be characterized in detail. These data have been shown in our previous studies [11,12]. The precursor was melt spun to fiber form at 403-453K. The diameters of the spun fibers were measured by Digital Microscope. For the chemical vapor curing, exposure of spun fibers to $SiCl_4$, $TiCl_4$ or 1.0 M BCl_3 in para-xylene solution at 299-309K was examined (Fig. 1). The electron beam curing was performed with 2MeV beam with a dose rate of 0.79kGy/s. FT-IR spectra and TG curves on the cured fibers were analyzed. After the pyrolysis at 1273K, morphology of the fibers was observed by FE-SEM. In the cases of the $SiCl_4$ curing and electron beam curing, tensile strength of the resulting monofilaments was measured with a gauge length of 10 mm. Morphology change of the obtained Si-O-C fibers after high temperature exposure was observed by FE-SEM.

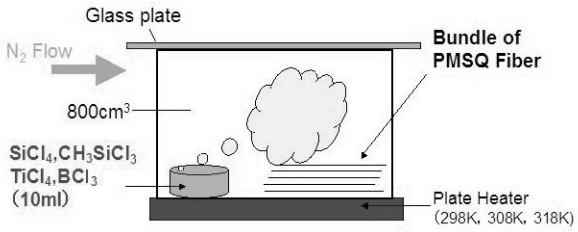

Fig. 1. A image of metal chloride vapor curings.

Results and Discussion

Melt spinning process was successful at 403-453K with a spinning speed of 10m/s (Fig. 2). The averaged diameter of the spun fibers depended on melt spinning temperature and holding time (Table 1). As the temperature rising, melt spinnability of PMSQ was improved. Beyond 423K, however, melt hardening started to prevent the spinning process, and averaged diameter of the fiber became to be dispersed. It is consistent with reported thermosetting character of PMSQ. In order to diminish such melt hardening effect, reduction of holding time at appointed melt spinning temperature was effective.

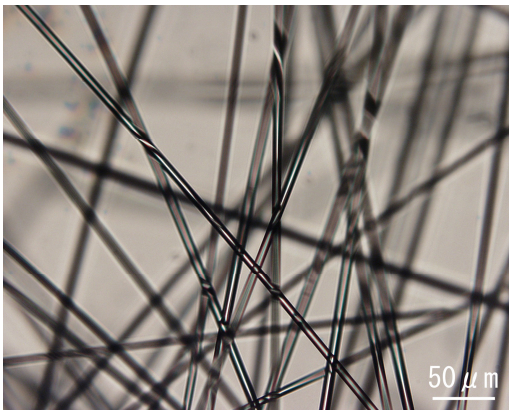

Fig. 2. An optical micrograph of melt spun PMSQ fiber.

Table 1. An averaged diameters of melt spun PMSQ fiber.

Melt Spinning Temperature	Holding Time	Averaged Diameter
403K	60min	30.0±7.1 μm
423K	60min	25.4±4.2 μm
423K	20min	16.8±1.4 μm
453K	60min	51.7±6.4 μm

Since softening temperature of PMSQ is low, thermal oxidation curing usually adopted for PCS fiber is not available for PMSQ. Curing by $SiCl_4$ or BCl_3 vapors at room temperature were available for keeping fiber form after pyrolysis. In the case of $TiCl_4$ vapor, higher temperature, 543K, was necessary to perform the curing. It is probably due to low vapor pressure of $TiCl_4$ as compared with $SiCl_4$ and BCl_3. The fiber surface, cured with BCl_3 or $TiCl_4$ was, however, covered by oxide base particles (Fig. 3. (a), (b), (c)). The particles sometimes made bridges between monofilaments. In these cases, tensile tests on monofilaments were impossible. The fiber obtained with $SiCl_4$ curing and 1273K pyrolysis showed smooth surface and tensile tests on monofilaments were possible. The averaged strength was 0.30±0.13GPa.

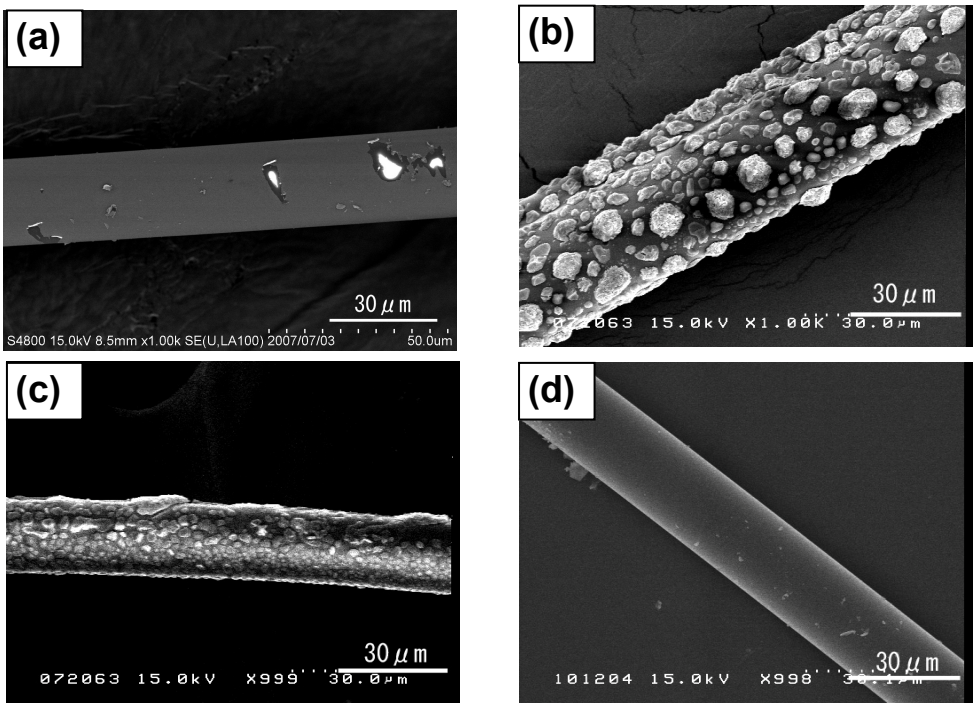

Fig. 3. SEM images of Si-O-C (or Si-O-C-M) fibers after 1273K pyrolysis: (a) $SiCl_4$ curing, (b) TiCl4 curing, (c) BCl3 curing and (d) Electron beam curing.

Electron beam curing in an air flow was also available for curing (Fig. 3. (d)). Although use of the electron beam curing is not appropriate for our final purpose to produce low cost fiber, it is useful probe to investigate theoretical properties of Si-O-C fibers derived from PMSQ. The measured mechanical properties of the fiber strongly depended not only on spun diameter, but also on total dose of irradiation (Fig. 4). At total dose with 10.3 MGy, the tensile strength of the fiber showed maximum of 0.73±0.28GPa with an averaged diameter of 16.8 μm.

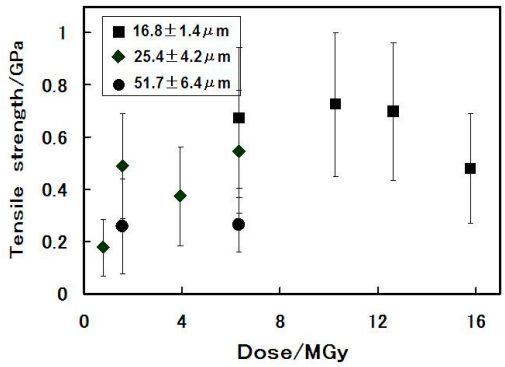

Fig. 4. Tensile strength of Si-O-C fibers derived from EB cured PMSQ fibers.

Figure 5 shows the micrographs of the obtained Si-O-C fibers (with $SiCl_4$ curing) after exposure for oxygen-gas burner. These images are compared with that of high purity silica fibers after exposure. Even after 20min exposure, the Si-O-C showed slight fusion, while pure silica fibers were completely melted down just after 10sec.

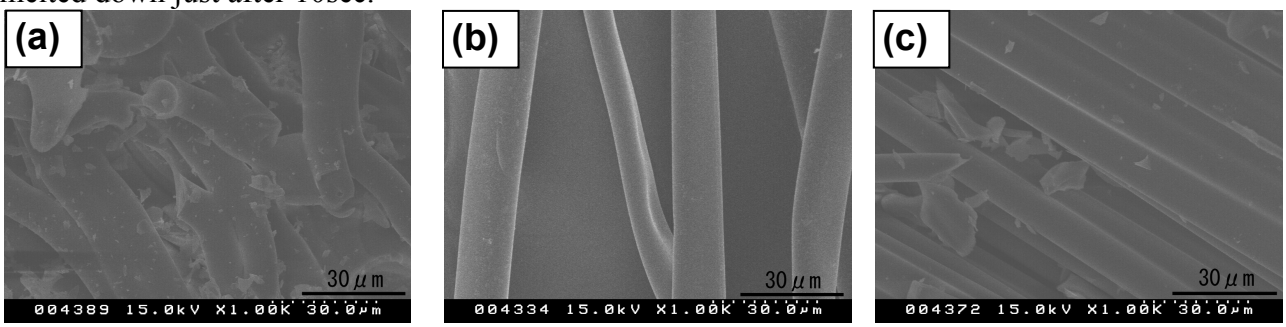

Fig. 5. SEM images of SiO_2 fiber or Si-O-C fiber ($SiCl_4$ curing) after oxygen-gas flame exposure: (a) SiO_2 fiber after 10s exposure, (b) Si-O-C fiber after 1min exposure, (c) Si-O-C fiber after 20 min exposure.

Summary

The average and distribution of spun PMSQ fiber diameter are strongly influenced by melt spinning temperature and holding time. Tendency is consistent with the reported thermosetting character of PMSQ. The vapors of $SiCl_4$ and 1.0 M BCl_3 in p-xylene solution are effective for curing even at room temperature. In a case of $TiCl_4$, higher temperature 309K is required. The tensile strength measurement is possible only in the case of $SiCl_4$, and the obtained value at present is 0.30±0.13GPa. Electron beam curing in an air flow is also effective to perform the fiber curing. In this case, the strength of 0.73±0.28GPa is obtained with a total dose of 10.3MGy. The heat resistivity of obtained Si-O-C fiber is far higher than that of pure silica fiber.

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