Preceramic Polymer-Derived SiOC Fibers by Electrospinning

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ABSTRACT: Silicon oxycarbide (SiOC) fibers with different chemical compositions were successfully fabricated by electrospinning a mixture of polyvinylpyrrolidone (PVP) and commercially available polymethylsilsesquioxane (MK) or polymethylphenylsilsesquioxane (H44) preceramic polymers, followed by cross-linking and pyrolysis at 1000°C in Argon. The influence of the processing procedure (solvent selection, cross-linking catalyst and additives) on the morphology of the produced fibers was investigated. For the MK/isopropanol system, the introduction of 20 vol% N,N-dimethylformamide (DMF) enabled to decrease the diameter of the as-spun fibers from 2.72 ± 0.12 μm to 1.65 ± 0.09 μm. For the H44/DMF systems, beads-free fibers were obtained by adding 50 vol% choloroform. After pyrolysis, the resultant SiOC fibers derived from MK and H44 resins possessed uniform morphology, with an average diameter of 0.97 ± 0.07 μm and 1.07 ± 0.08 μm, respectively. Due to their different chemical compositions, the MK-derived and H44-derived SiOC ceramic fibers could find different potential applications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39836.

INTRODUCTION

Electrospinning has been extensively explored as a simple and versatile method for the fabrication of continuous fibers with diameters ranging from tens of micrometers to a few nanometers.[1–3] In the past, this technique was limited to the production of thin fibers from organic polymers, due to the strict requirements that the physical properties of the electrospinning solution had to satisfy in order for the process to occur producing fibers with uniform morphology. Recently, researchers reported the successful fabrication of ceramic fibers by a combination of electrospinning and other methods (e.g. sol–gel and co-precipitation).[4–6] Normally, the production of ceramic fibers by electrospinning consists of three procedures: 1) preparation of the solution containing the ceramic precursor, 2) electrospinning of the prepared solution into polymer/inorganic composite fibers, and 3) calcination of the composite fibers to remove the polymer and to obtain the desired ceramic phase.[4] In addition to the conventional fiber mats, fibers with complex architectures, such as core–shell fibers, porous fibers, hollow fibers or fibers aligned along different ordered patterns can also be produced by electrospinning using various electrospinning setups.[7–9]

Silicon oxycarbide (SiOC) is an amorphous covalent ceramic material whose composition can be expressed as $SiC_xO_{2(1-x)} + yC_{free}$,

where $SiC_xO_{2(1-x)}$ refers to the amorphous silicon oxycarbide network and C_{free} is free carbon (i.e., carbon not bonded to Si or O atoms).[10–12] Because of the carbon, which can be part of the silicon-oxygen network or present as a separate phase, SiOC ceramics possess enhanced thermal, mechanical, and chemical properties compared to pure silica ceramics.[13,14] Besides dense bulk components,[15] SiOC ceramics with other shapes, such as foams,[16,17] microtubes[18] or fibers,[19,20] have also been successfully fabricated to meet the demands of different applications. SiOC fibers have been mainly prepared by mechanical spinning from a viscous melt or a sol–gel solution. Kita[21] reported the preparation of SiOC fibers by melt spinning from a polymer blend of polycarbosilane (PCS) and 15 wt % of polyhydromethylsiloxane (H-oil), producing fibers with a diameter, after pyrolysis, of about 30 μm. In Ruan's work[22] the polysiloxane fibers were drawn from a sol–gel system of tetraethoxide (TEOS) and vinyltrimethoxysilane using a glass bar, and then pyrolyzed into SiOC fibers with a diameter of about 26 μm. When fibers with a smaller diameter are desired, electrospinning should be used. This approach has already been investigated for some classes of preceramic polymers, such as polycarbosilane, polysilazane or polyborazine to prepare SiC,[23–25] SiCN[26] or BN[27] fibers, although the literature is still rather scarce. A few papers have also dealt with the fabrication of SiOC fibers by electrospining.[28,29] However, few details concerning the reasons for selecting specific experimental conditions for the electrospinning process were typically given and

Table I. Molecular Properties of MK and H44 Resins

	Poly methyl-silsesquioxane (MK resin)	Poly methylphenyl-silsesquioxane (H44 resin)
Chemical formula	$[(CH_3)_{0.96}(OR)_{0.04}SiO_{1.5}]_n$	$[(C_6H_5)_{0.62}(CH_3)_{0.31}(OR)_{0.07}SiO_{1.5}]_n$
Crosslinking groups	OR= -OH and $-OC_2H_5$	OR= -OH and $-OC_2H_5$
M_w (g/mol)	9100	2100
M_w/M_n	3.6	1.8

the finest fiber diameter size achieved was ∼3.5 to 5 μm. In this paper, we discuss in detail the whole fabrication procedure, including the selection of solvent, additives and cross-linking catalyst and the optimization of fiber morphology, reporting the production of ∼1 μm SiOC fibers from commercially available silicone resin polymers. The SiOC fiber mats could be used for catalyst support and filtration purposes in harsh environments and high temperature.[4,30] Furthermore, it is also possible to produce the carbon mesoporous fibers by chlorinating the SiOC fibers[31] or mullite fibers by introducing alumina nanoparticles in SiOC fibers.[32]

EXPERIMENTAL

Chemicals

Two different commercially available silicone resins (MK and H44, Wacker-Chemie GmbH, München, Germany) were used as the preceramic precursors. The molecular properties of MK and H44 resins were shown in Table I.[33,34] SiOC ceramics obtained from the H44 silicone resin possess a higher carbon content than those from the MK silicone resin.[34] Isopropanol, chloroform and N,N-dimethyl formamide (DMF) were used as the solvent; polyvinylpyrrolidone (PVP, M_w = 1.300.000 Da), Triton X-100 surfactant and sodium chloride (NaCl) were used as the additives; Zr containing catalyst (Zr-acetylacetonate) and Sn containing catalyst (dibutyltin dilaurate) were used as the cross-linking catalyst for H44 and MK resin, respectively. All chemicals were purchased from Sigma-Aldrich apart from the Sn containing catalyst (DABCO T12N), purchased from Air Products Chemical.

Electrospinning and Pyrolysis

Although both MK and H44 resins are methylsilicones, they show different solubility in some solvents due to their difference at the molecular level. For example, H44 resin possesses a high solubility in DMF, while MK is insoluble in DMF. Therefore, different solvents were selected for the MK and the H44 resins.

To successfully electrospin the MK resin, a mixture of it and PVP polymer (75/25 weight ratio) was dissolved in isopropanol (total polymer concentration = 30 wt %). 0.5 wt% Sn containing catalyst was added to the solution in order to maintain the fiber shape during the cross-linking and pyrolysis processes. The solution was loaded into a 5 mL syringe fitted with a 0.7 mm diameter stainless steel needle and fed at 0.5 mL/h with a syringe pump (NE-300, New Era Pump Systems, USA). Electrospinning was carried out at a voltage of 10 kV using a DC power supply (ES100R-20W, Kansai Elctronics, Japan). An aluminum plate was used as the collector, and the nozzle-collector distance was 12 cm. In addition, a solution of isopropanol con-

taining only 60 wt % of pure MK resin was tested to verify the role of PVP. In order to decrease the resultant fiber diameter, the physical or electrical properties of electrospining solution were adjusted following three different routes: (1) adding 0.5 wt % Triton X-100 surfactant; (2) using an isopropanol/water mixture at 99/1 weight ratio containing 0.1 wt % NaCl as the solvent, instead of pure isopropanol solvent; (3) using an isopropanol/DMF mixture at 80/20 volume ratio as the solvent, instead of pure isopropanol solvent. When following these three routes, all the other electrospining parameters were held constant.

The H44 resin was mixed with the PVP polymer at 75/25 weight ratio and dissolved in DMF (the total polymer concentration = 35 wt %), and 4.0 wt % Zr containing catalyst was added. The electrospinning parameters were +10 kV working voltage, 0.5 mL/h feeding rate and 12 cm working distance (aluminum plate collector). A solution of pure DMF containing 60 wt % H44 was also tested as previously mentioned for the MK system. Furthermore, fibers were also electrospun using a mixture of DMF and chloroform at different volume ratios (70/30, 50/50, and 30/70) with other parameters being kept equal. The catalyst type and amount used for MK and H44 resin were optimized experimentally in separate experiments.

After the spinning process, the as-spun MK/PVP and H44/PVP fibers were cross-linked at 200°C for 1 h in air (heating rate = 5°C/min), to make them infusible. Then the fibers were pyrolyzed in an alumina tube furnace under flowing argon at 1000°C, with a heating rate of 2°C/min and a holding time of 2 h.

Characterization

The morphology of the products was examined by a scanning electron microscope (SEM; JSM-6490, Jeol Italia, Italy)) after gold coating, and the chemical composition of the pyrolyzed SiOC fibers was analyzed by Energy Dispersive X-ray Spectroscopy (EDS). For each type of electrospun fibers, 50 fibers

Table II. Solubility of MK Resin, H44 Resin and PVP in Different Solvents

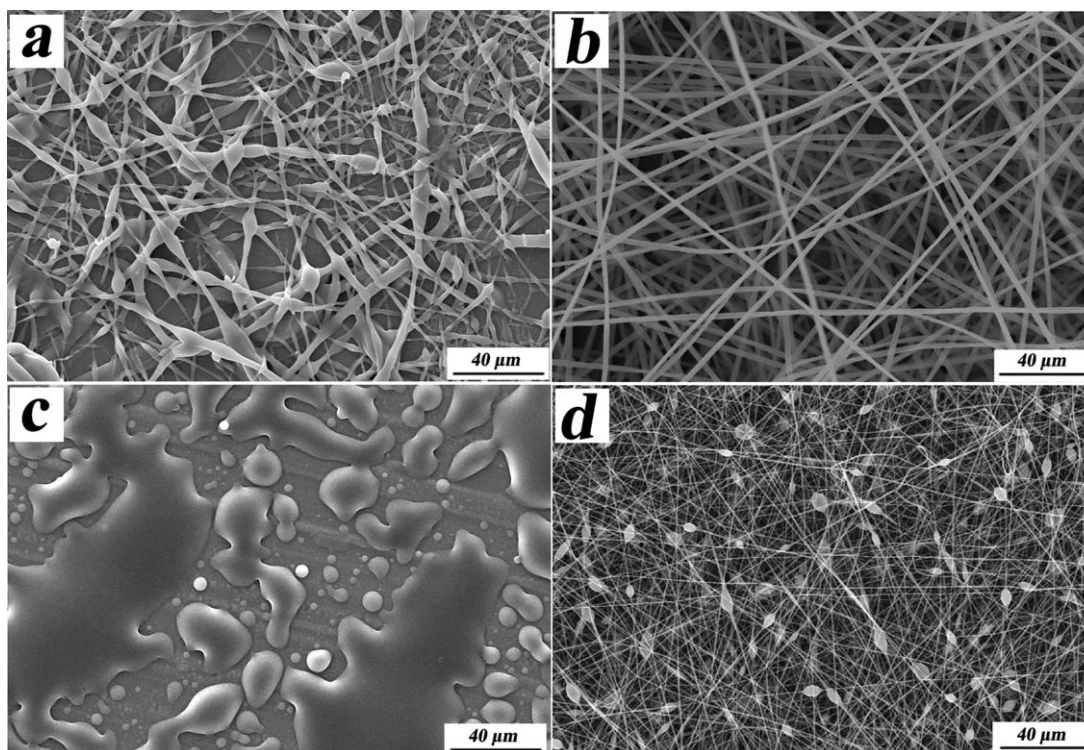|	Solvent				
Solute	Isopropanol	DMF	Acetone	Ethanol	Chloroform
MK	High	Insoluble	Partial	Partial	Partial
H44	High	High	Partial	Partial	Partial
PVP	High	High	Insoluble	High	High

Figure 1. SEM micrographs of as-spun relics from solutions of: (a) MK resin in isopropanol, (b) MK/PVP mixture in isopropanol, (c) H44 resin in DMF, and (d) H44/PVP mixture in DMF.
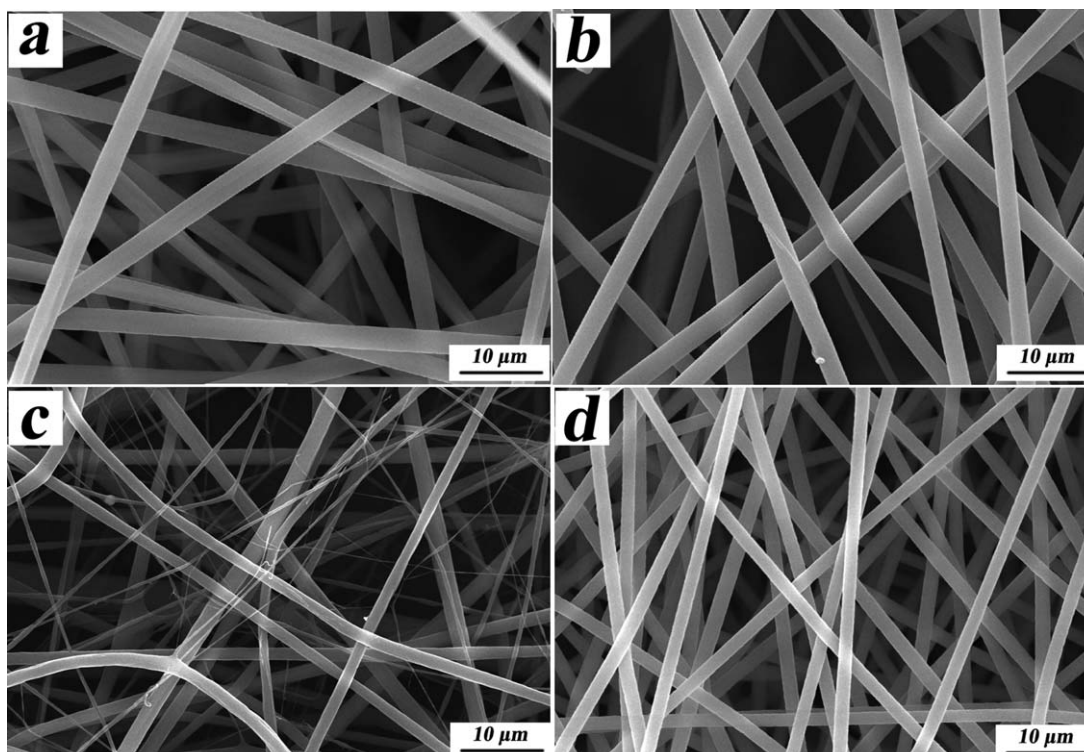

Figure 2. SEM micrographs of as-spun MK/PVP fibers produced from: (a) a pure isopropanol solvent, (b) pure isopropanol solvent with addition of 0.5 wt % Triton X-100 surfactant, (c) an isopropanol/water solvent mixture at 99/1 weight ratio containing also 0.1 wt % NaCl, and (d) an isopropanol/DMF solvent mixture at 80/20 volume ratio.

Table III. Average Diameters for As-Spun MK/PVP Fibers Electrospun in Different Conditions

Solvent	Additive	Diameter (μm)
Pure isopropanol	-	2.72 ± 0.12
Pure isopropanol	0.5 wt % Triton X-100 surfactant	2.25 ± 0.27
Mixture of isopropanol/water at the weight ratio of 99/1	Wt % NaCl	1.51 ± 0.25
Mixture of isopropanol/DMF at the volume ratio of 80/20	-	1.65 ± 0.09

were counted to calculate the average fiber diameter from the SEM image. Fourier Transform infrared (FTIR) spectra were collected at a resolution of 4 cm^{-1} using a Nicolet 5700 spectrometer (Thermo Fisher Scientific, USA). The thermal behavior of the PVP powders, cross-linked MK/PVP fibers, and cross-linked H44/PVP fibers was investigated by heating under argon atmosphere at 10°C/min using a thermogravimetric analyser (DTA/TGA, STA409, Netzsch Gerätebau GmbH, Germany). X-ray diffraction analysis (XRD) was conducted on the polymer-derived-ceramic fibers after pyrolysis (Bruker D8 Advance, Bruker Italia, Italy, Cu Kα radiation, step scan 0.02°, 2 sec/step).

RESULTS AND DISCUSSION

Selection of Polymer Additive and Solvent

It is possible to obtain the ceramic fibers by directly electrospinning a sol solution that only contains an inorganic precursor (metal alkoxides or metal salts) and a solvent. However, the requirement for the rheological properties of electrospinning solution to fabricate a continuous fiber with a uniform diameter distribution is very strict.[5] To facilitate the process, a polymer is often introduced into the solvent to adjust the rheological properties.[4–6] In this work, PVP was used because it has a high solubility in a variety of solvents and good compatibility with many metal alkoxides.

Selecting an appropriate solvent is also of great importance for electrospining. Table II reports the solubility of MK, H44 and PVP in some common solvents. Luo[35] suggested that for MK resin the solvent of lower solubility can be better suited for making good electrospinnable solutions than solvents of high solubility. However, in our work, due to the addition of the PVP polymer, the electrospinnability was mainly determined by the PVP concentration. Therefore, a solvent with a high solubility for PVP was more suitable for successful electrospinning. On the other hand, in consideration of the large loss weight of the silicon resin during the polymer-to-ceramic transformation, it is better to select the solvent that also shows a high solubility for the MK or H44 resins, in order to increase the preceramic content. In this case, isopropanol and DMF were selected as the solvent for MK and H44, respectively. It should be mentioned
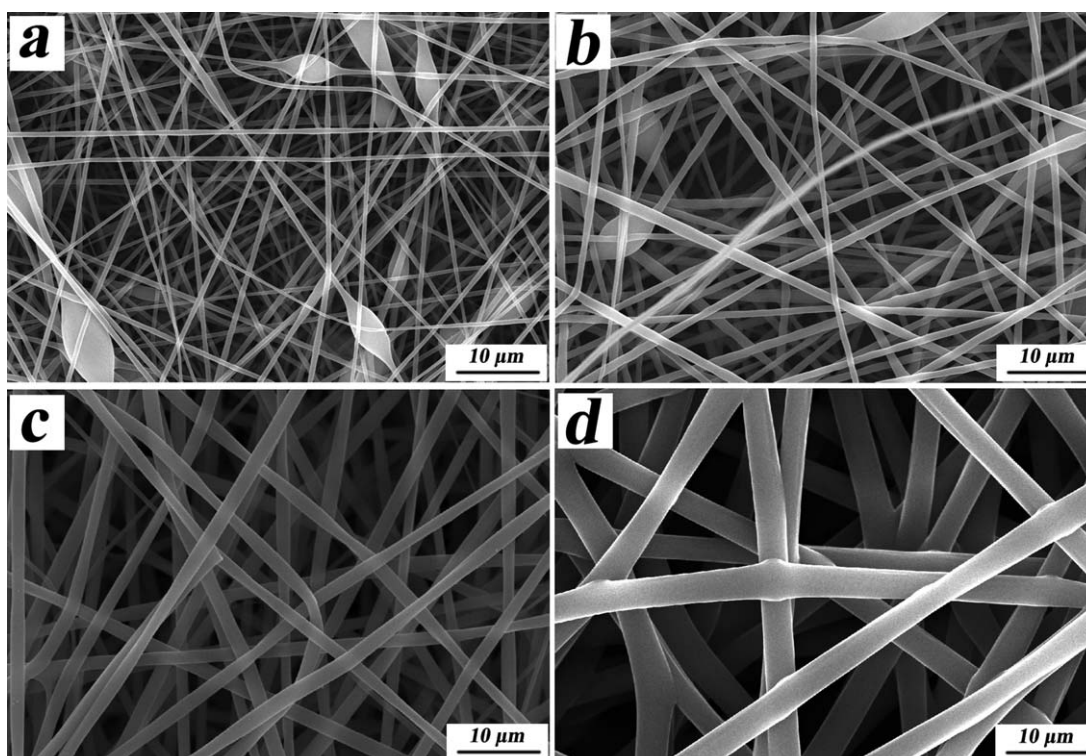

Figure 3. SEM micrographs of as-spun H44/PVP fibers from mixtures of DMF and chloroform in different volume ratios: (a) 100/0, (b) 70/30, (c) 50/50, and (d) 30/70.

Table IV. Average Diameters for As-Spun H44/PVP Fibers Electrospun from Mixtures of DMF and Chloroform in Different Volume Ratios

DMF/chloroform (volume ratio)	100/0	70/30	50/50	30/70
Diameter	491 ± 94 nm	$0.91 \pm 0.16\ \mu m$	$1.61 \pm 0.16\ \mu m$	$3.35 \pm 0.26\ \mu m$

that although isopropanol also shows a high solubility for both H44 and PVP, H44 and PVP become incompatible when they simultaneously dissolved in isopropanol. Therefore, isopropanol was not found to be suitable for the H44 resin.

Figure 1 shows the effect of addition of PVP on the morphology of the electrospun fibers (before pyrolysis). As expected, in contrast to the fibers produced from MK resin without PVP, which possessed a rough surface, an irregular cross-section and a non uniform diameter [Figure 1(a)], the addition of PVP led to uniform fibers (average diameter $2.72 \pm 0.12\ \mu m$) with good, smooth morphology [Figure 1(b)]. When using the pure H44 preceramic polymer, it was impossible to even produce fibers, at least in our experimental conditions (voltage and concentration) adopted [see Figure 1(c)]. The addition of PVP, dissolved in DMF, led to the production of continuous H44/PVP fibers with a diameter of 491 ± 94 nm [see Figure 1(d)]. Some beads formed along the H44/PVP fibers, due to the poor evaporability of the DMF solvent.[36] Moreover, the diameter of as-spun H44/PVP was much smaller than that of as-spun MK/PVP fiber, and this can be attributed to the low surface tension and high dielectric constant of the DMF solvent.[37] The amount of PVP added was optimized

experimentally and the weight ratio of preceramic polymer/PVP was fixed at 75/25. If the content of PVP was too low, the morphology of the electrospun fibers was not uniform, like the fibers in Figure 1(a), due to the poor electrospinnability. In addition, a high content of PVP would result in a high weight loss during the polymer-to-ceramic transformation.

Optimization of the Fiber Morphology

Electrospinning is quite a complicated process, in that there are numerous parameters that can influence the morphology of the resultant fibers. These parameters may be broadly classified into two types: electrospinning solution parameters (including surface tension, viscosity, and electrical properties) and operating parameters, which include the applied voltage, feeding rate, nozzle-collector distance, and ambient conditions (such as temperature and relative humidity).[3] Therefore, it is possible to optimize the fiber morphology by adjusting some of these parameters.

In the MK resin system, as mentioned before, the average diameter of the as-spun MK/PVP fibers produced using the initial experimental parameters was about $2.72 \pm 0.12\ \mu m$ [Figure 2(a)].
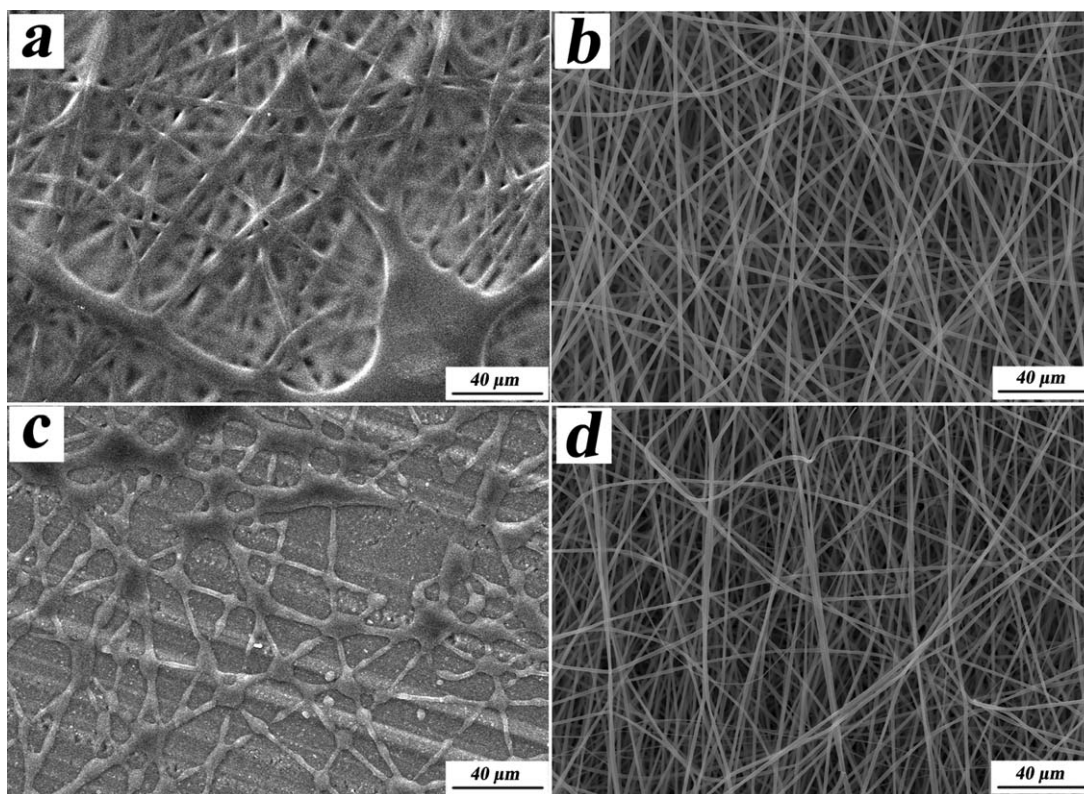

Figure 4. SEM micrographs of cross-linked MK/PVP fibers without (a) and with catalyst (b), and cross-linked H44/PVP fibers without (c) and with catalyst (d). Fibers cross-linked at 200°C for 1 h.
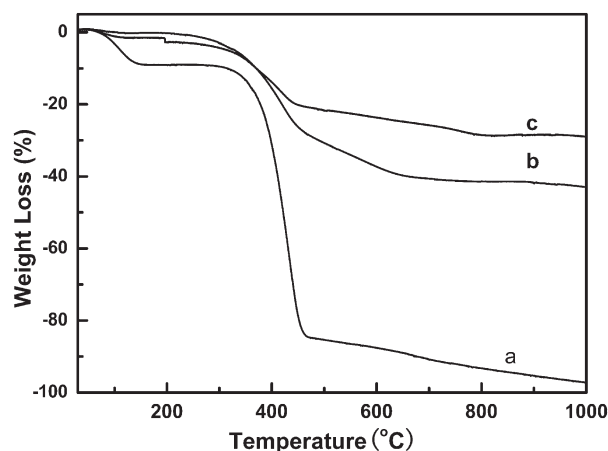
Figure 5. TGA analysis data for: (a) PVP powders, (b) cross-linked H44/PVP fibers, and (c) cross-linked MK/PVP fibers.

We therefore proceeded to investigate how to reduce the fiber diameter. After some screening experiments, we found that the electrospining window for the MK/isopropanol system was quite narrow, which means that the electrospinnability of this system is very sensitive to the operating parameters, such as working voltage and nozzle-collector distance. Therefore, it is difficult to reduce the fiber diameter by adjusting the operating parameters. Compared to the operating parameters, the electrospinning solution parameters, especially the surface tension, dielectric constant, and electrical conductivity, can influence the fiber diameter more effectively. Normally, reducing the solution surface tension or increasing the solution dielectric constant or electrical conductivity is an effective way of decreasing the fiber diameter. Triton X-100 surfactant has been used in many papers to lower the surface tension of electrospinning solution.[38] Figure 2(b) shows the morphology of as-spun fibers with the addition of 0.5 wt % Triton X-100, revealing that the fiber diameter decreased slightly to 2.25 ± 0.27 μm. Addition of salt is another effective way to produce fine fibers, because of the increase of solution conductivity with consequent increase of the surface charge density of the solution jet.[39] NaCl is insoluble in isopropanol, and therefore we added some water to the isopropanol; the final electrospinning solvent was then an isopropanol/ water mixture at 99/1 weight ratio, containing 0.1 wt % NaCl. As shown in Figure 2(c), the average diameter of the as-spun MK/PVP fibers electrospun from the solution with the addition of NaCl decreased to 1.51 ± 0.25 μm. However, some ultrafine fibers were also present, and this was due to the repeated spraying of the fiber jets.[40,41] In addition to electrical conductivity, the dielectric constant of the electrospinning solution plays also an important role in influencing the diameter of resultant fibers. N,N-dimethylformamide (DMF), possessing a low surface tension (35.2 mN/m at 25°C) and high relative dielectric constant (36.7 at 20°C), has been reported in several papers to enable the production of ultrafine fibers.[36,42] Although the MK resin was insoluble in DMF (Table II), both isopropanol and PVP show good compatibility with DMF. Therefore, a small quantity of DMF was introduced in isopropanol to adjust the surface tension and dielectric constant of the electrospinning solution. After several trials, the concentration of introduced DMF was fixed at 20 vol %, because although the

fiber diameter could further decrease for a higher concentration, the diameter distribution would become much wider due to the incompatibility between MK and DMF. The as-spun MK fibers electrospun from the mixed solvent (isopropanol/DMF ratio of 80/20 volume ratio) had a diameter of 1.65 ± 0.09 μm, which constitutes a size reduction of 39% [see Figure 2(d)]. In addition, the fibers exhibited a narrower diameter size distribution than those fabricated using the previous two experimental conditions (see Table III). Therefore, the mixture of DMF and isopropanol with a 20/80 volume ratio was selected as the final solvent for the subsequent electrospinning experiments of MK/PVP fibers.

As mentioned before, for as-spun H44/PVP fibers, due to the high boiling point (153°C) and low vapor pressure (0.38 kPa at 20°C) of the DMF solvent, the formation of some beads was observed along the fibers [see Figure 3(a)]. To solve this problem, chloroform, which has a low boiling point (61.3°C) and a high vapor pressure (21.2 kPa at 20°C), was added to
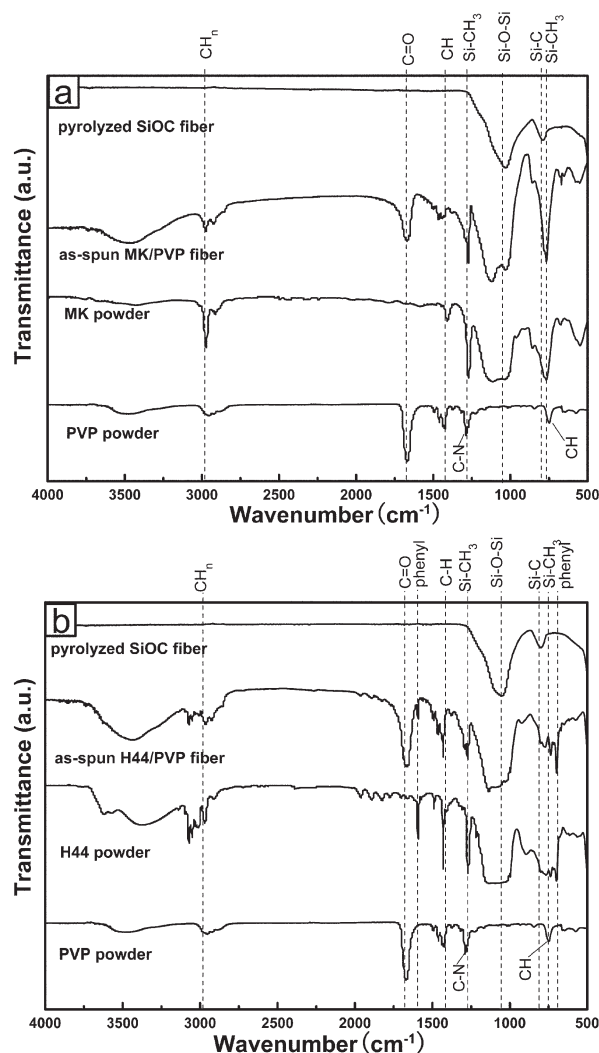

Figure 6. FTIR spectra of starting materials and electrospun fibers in: (a) the MK preceramic polymer system, and (b) the H44 preceramic polymer system.
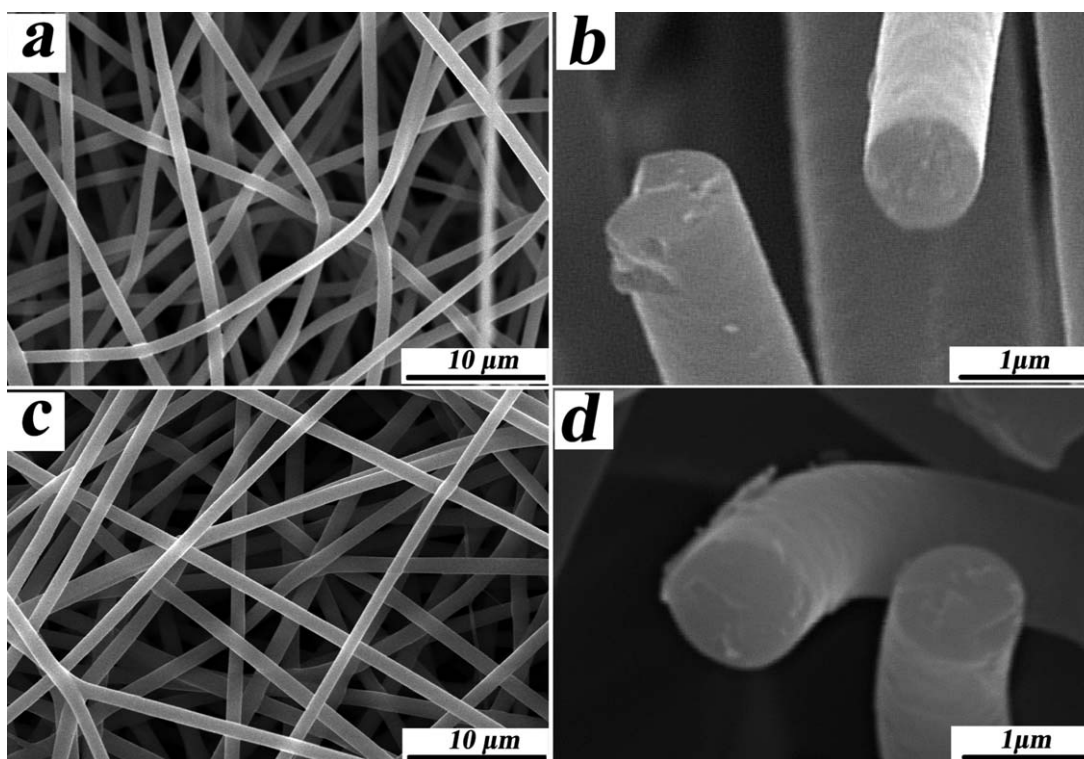
Figure 7. SEM micrographs of SiOC fibers from the pyrolysis of: MK/PVP fibers (a and b), and H44/PVP fibers (c and d).

DMF, in order to improve the solvent evaporability. Electrospun fibers were prepared by using mixtures of DMF and chloroform in the volume ratios of 70/30, 50/50, and 30/70. The scanning electron micrographs show that at the highest ratio of the solvent mixture (DMF/chlorofrom at 70/30 volume ratio), the bead defects were still generated [see Figure 3(b)], but as the ratio gradually decreased to 50/50, no beads could be observed [see Figure 3(c)]. However, the fiber diameter increased gradually with the increase of the chloroform concentration (see Table IV), because of the increase of the dielectric constant of the mixture (relative dielectric constants at 20°C of chloroform and DMF are 4.8 and 36.7, respectively). Therefore, in order to produce fibers from the H44 resin with a small diameter and without beads, a

solvent mixture of DMF/chloroform at 50/50 volume ratio was selected as the final solvent for the subsequent electrospinning experiments of H44/PVP fibers.

Cross-Linking and Pyrolysis

After shaping, a preceramic polymer component usually needs to be cross-linked in order to be transformed into a thermoset capable of retaining its shape during the subsequent heating (polymer-to-ceramic transformation).[12] Depending on the type of shaping method adopted and the component fabricated, cross-linking can occur during the shaping process,[43] or a post-processing chemical treatment can be applied,[18] or a large amount of filler particles can be added to the preceramic
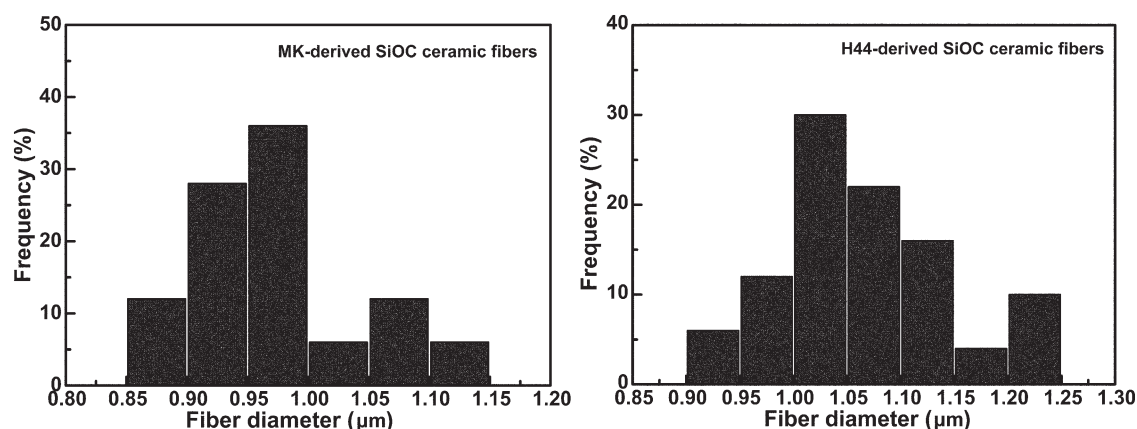

Figure 8. Fiber diameter distributions of MK-derived and H44-derived SiOC fibers.
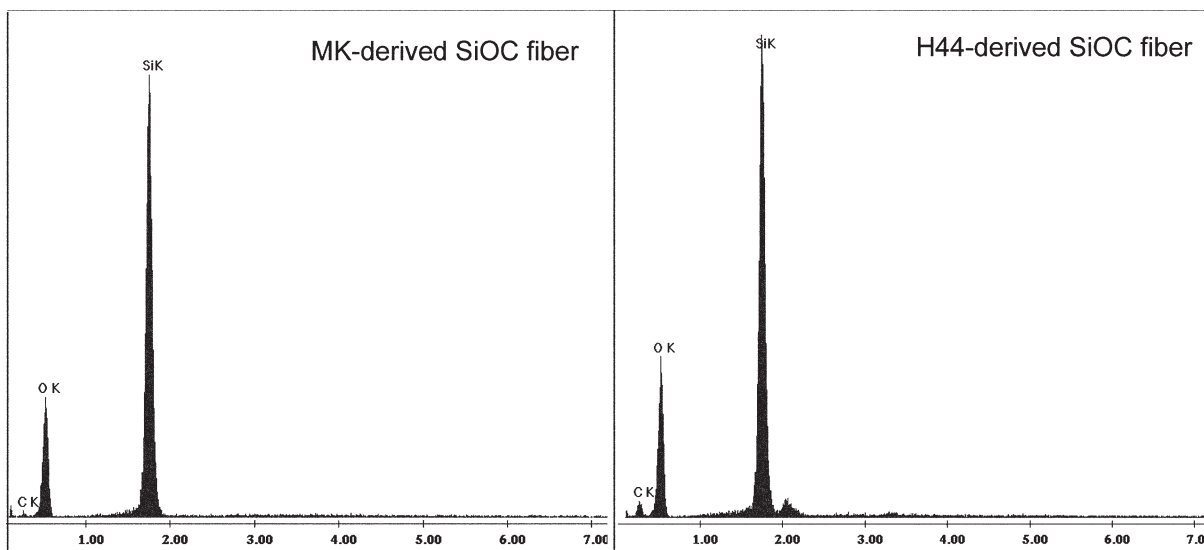
Figure 9. Energy-dispersive X-ray spectrums of MK-derived and H44-derived SiOC fibers.

polymer to offer sufficient support to the polymeric matrix during heating;[44] therefore, in these cases, the addition of a cross-linking catalyst is not necessary. However, for electrospun SiOC fibers, a cross-linking catalyst, which lowers the cross-linking temperature and reduces the decrease in the polymer viscosity with increasing processing temperature,[45] must be introduced in order to maintain the fiber shape during the cross-linking process. Figure 4(a,c) clearly shows that, without the addition of a catalyst, both MK/PVP and H44/PVP fibers melted after heating at a temperature above the glass transition temperature of the silicone resins (which is of the order of ∼50°C). In contrast, the MK/PVP [Figure 4(b)] and H44/PVP (Figure 4d) fibers produced with the addition of a suitable catalyst (Sn containing catalyst for MK resin and Zr containing catalyst for H44 resin) maintained a perfect morphology after cross-linking.

Differently from the electrospinning of polymer fibers, the fabrication of ceramic fibers often requires an additional process that is a high temperature treatment to remove the added polymer (when present) and to obtain the desired ceramic phase. Figure 5 shows the TGA data for the PVP powder, cross-linked H44/PVP fibers and cross-linked MK/PVP fibers (heating in Argon atmosphere). As shown in Figure 5(a), PVP was almost completely eliminated after pyrolysis at 1000°C, and the main weight loss occurred at around 450°C. For the composite fibers, the weight loss occurring between 400 and 800°C was due to the polymer-to-ceramic transformation, involving the redistribution reactions between Si—O and Si—C bonds as well as the decomposition of organic moieties (such as methyl, ethyl and phenyl groups).[11,12] Because the fibers were cross-linked at 200°C, they displayed very limited weight loss below 400°C.

The FTIR spectra for the samples (Figure 6) clearly indicate the transformations of MK or H44 resins to SiOC ceramics during the pyrolysis process. In both MK and H44 system, all the characteristic absorption peaks of PVP at 1670 cm^{-1} and 1290 cm^{-1} corresponding to the C=O and C—N on the pyrrolyl ring[46,47]

disappeared after pyrolysis at 1000°C, further supporting the burn-off of PVP in pyrolyzed fibers, which is consistent with the TGA analysis. On the other hand, the disappearance of the signal related to CH_n at 3500−2900 cm^{-1}, Si—CH_3 at 1270 cm^{-1}, C—H in Si—CH_3 at 760 cm^{-1}, and phenyl at both 1590 cm^{-1} and 696 cm^{-1} (only existing in H44 resin) after pyrolysis confirmed the conversion of the preceramic MK or H44 resin to SiOC ceramics. The formation of SiOC ceramic fibers is further proved by the appearance of the Si—O—Si peak at 1030 cm^{-1} and of the Si—C peak at 790 cm^{-1}.[45] XRD analysis performed on selected samples (not reported here for the sake of brevity), confirmed the formation of an amorphous ceramic (hump centered at around 21°, typical for SiOC materials).[12,13]

The microstructure of SiOC fibers obtained from the pyrolysis of MK/PVP and H44/PVP as-spun fibers is shown in Figure 7 and the fiber diameter distributions of the MK-derived and H44-derived SiOC fibers are shown in Figure 8. The nonwoven fibrous network was preserved after pyrolysis, and both MK and H44-derived fibers appear to have a small average fiber diameter and narrow size distribution (0.97 ± 0.07 and 1.07 ± 0.08 μm, respectively). Furthermore, their cross-sections do not contain any macroscopic defect [see Figure 7(b,d)]. The SiOC fibers produced in this work exhibit both a smaller average diameter and a more controlled morphology than those previously reported by previous literature.[21,22,28,29,48]

Silicon oxycarbide (SiOC) is an amorphous covalent ceramic material whose composition is not fixed and is mainly determined by the starting material. The chemical composition of the pyrolyzed SiOC fibers was analyzed by EDS (Figure 9). The quantification analysis shows that the atomic proportions of MK-derived SiOC fiber was 34.6% Si, 52.5% O and 12.9% C, while that of H44-derived SiOC fiber was 25.8% Si, 48.6% O, and 25.6% C. The carbon content of H44-derived SiOC fibers was much higher than that of MK-derived SiOC fibers, resulting

from the molecular composition difference between MK resin and H44 resin.[34] Due to the different chemical composition, the MK-derived and H44-derived SiOC fibers can find different potential applications. For example, the H44-derived SiOC fibers with high carbon content were more suitable to be used to prepare the carbon mesoporous fibers using chlorination method,[31] while the MK-derived SiOC fibers with high silicon content can be used to produce mullite fibers using a similar strategy we reported,[32] provided that the electrospinning solution containing the preceramic polymer still maintains its spinnability after a significant amount of nanosized particles are added and the fiber shape could maintain after the sintering in air. Apart from these mentioned applications, the resultant SiOC fiber mats could also be used, instead of ceramic foams, for filtration purposes.[30] Furthermore, a variety of nanoparticles could be added to the electrospinning solution, in order to produce fibers with well-defined functionalities (e.g., for catalysis or sensing).[49]

CONCLUSIONS

This article reported a detailed process for the fabrication of SiOC fibers with homogeneous morphology by electrospinning of solutions containing two commercially available methylsilicones. PVP was introduced to improve the electrospinnability of the preceramic solutions. For the MK/isopropanol system, the effect of the solution surface tension, electrical conductivity and dielectric constant on the variation of the fiber diameter was investigated. The introduction of 20 vol% DMF in pure isopropanol solvent was the most effective approach, enabling to reduce the as-spun fibers diameter from 2.72 ± 0.12 μm to 1.65 ± 0.09 μm. For the H44/DMF system, beads-free fibers were obtained by adding 50 vol % choloroform, and the resultant as-spun fiber diameter was 1.61 ± 0.16 μm. The addition of a cross-linking catalyst was found to be necessary for maintaining the fiber shape during the polymer-to-ceramics heating process. After pyrolysis, both MK-derived and H44-derived SiOC fibers possessed homogeneous, defect free morphology, small average diameter size and narrow size distributions (0.97 ± 0.07 and 1.07 ± 0.08 μm, respectively). Because of the different chemical compositions, the MK-derived and H44-derived SiOC ceramic fibers had different potential applications.

ACKNOWLEDGMENTS

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