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Preparation and properties of silicon oxycarbide fibers

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Silicon oxycarbide fibers have been prepared from vinyl trimethoxysilane (VTMS) by a modified sol-gel method and with secondary cellulose acetate (SCA) as the fiber-forming aid. Its main advantage over a normal sol-gel fiber processing is that the spinning dope remains spinnable for a long period of time. The effect of the pre-hydrolysis of VTMS on the dope spinnability is studied. At $H_2O/VTMS = 4$, the resultant sol transforms into gel very quickly, unsuitable to obtain a spinnable dope; at $H_2O/VTMS = 2$, too much un-reacted VTMS exists in the sol, making the extruded fiber difficult to solidify; at $H_2O/VTMS = 3$, a dope with good spinnability, stability and high ceramic yield is obtainable. Pyrolysis at 1000°C in argon/5% hydrogen results in silicon oxycarbide fibers with the maximum tensile strength (940.0 MPa), moderate Young's modulus (63.2 GPa) and high carbon content (33.2%). © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Continuous inorganic fibers are widely used in advanced composites as reinforcements to improve strength, stiffness and toughness of polymers, metals or ceramics. Commercially available fibers include silicon carbide, alumina, boron, carbon and glass. Each of them has own merits and is suitable for certain applications. For example, silicon carbide fibers have excellent high temperature properties and are normally used to reinforce advanced ceramics. Alumina fibers retain strength only below 1200°C, so they find applications in metal or glass matrix composites. Boron and carbon fibers are outstanding for their high specific strength and specific modulus, but degrade rapidly above 500°C in oxidizing environments. All the four types of fibers are expensive, seriously limiting their widespread applications. Glass fibers are much cheaper, but they soften and lose reinforcing ability at ~500°C, so that they are usually used to reinforce polymers.

There exists a demand to produce a fiber combining the good mechanical properties of non-oxide fibers, the oxidation resistance of oxide fibers and the low cost of glass fibers. Silicon oxycarbide fiber is promising to meet these requirements. The first generation of silicon carbide fibers (Ceramic grade Nicalon), developed by Yajima *et al.* [1–3], was best defined as silicon oxycarbide fibers, since it contained more than 10% oxygen, intimately mixed with silicon and carbon at an atomic level. The oxygen was introduced during the oxidation curing stage. These fibers exhibit good mechanical properties and oxidation resistance at moderate temperature (<1200°C). However, the Nicalon route to silicon oxycarbide fibers has proven to be extremely costly, seriously limiting its application.

Pyrolyzing the hydrolysis products (gel) of organosilicon esters may also produce silicon oxycarbide phases [4–6]. The sol-gel technique has now developed into the most important route to prepare refractory fibers, especially oxide fibers, because it provides low processing temperature, high material purity and relatively low cost. Many oxide or mixed oxide fibers can be prepared by the sol-gel method, such as silica, alumina, zirconia and yttrium-aluminum garnet. The preparation usually includes the hydrolysis of organometallic esters for the formation of sol, aging the sol to increase the viscosity, dry spinning and pyrolysis in air. If the pyrolysis is carried out in a non-oxidizing atmosphere, for example nitrogen, phases other than oxides may be formed. One of the major problems of the sol-gel route to ceramic fibers is that only a very limited number of systems are suitable for fiber formation [7]. A spinnable sol must have appropriate viscosity, high sol stability, and the ability to solidify during spinning. Sols suitable for the formation of silicon oxycarbide phase usually have poor spinnability because of their difficulty in solidification. In this paper, the preparation of a silicon oxycarbide fiber by a modified sol-gel method is described. The readily available raw materials and the simple processing techniques promise low fiber production cost. These fibers may find application as reinforcements to complement commercial fibers.

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TABLE I I Dry spinning conditions

Spinneret, Number of holes/hole diameter (μm)	8/120
Calculated extrusion rate (m/min)	22.1
Drying temperature (°C)	70
Winding rate (m/min)	52

2. Experimental procedures

Vinyl trimethoxysilane (VTMS, chemical formulae $CH_2{=}CHSi(OCH_3)_3$, purchased from Aldrich) was used as the source of silicon and carbon, and secondary cellulose acetate (SCA, supplied by Shanghai Chemical Company) with an acetyl value of 52–55% as the fiber forming aid to facilitate the spinning.

VTMS was first hydrolyzed with acetone as solvent. The acetone/VTMS ratio was fixed at 6.5 by mole. Various water/VTMS ratios were studied. The hydrolysis was carried out by adding distilled water dropwise into VTMS under magnetic stirring. The hydrolysis reactions were highly exothermic, raising the temperature of the solution to ∼50°C. After the addition of water, the acetone was completely removed by heating at 50°C. The "complete" acetone removal was based on weight loss, assuming no water and VTMS evaporation. A part of the resultant sol was left undisturbed to allow for gelation. The rest of the sol was mixed with 15% SCA solution in acetone under mechanical stirring. The mix was further concentrated at 50°C to remove some of the acetone to give a spinnable dope. The dope was vacuum deaerated to remove any trapped bubbles prior to dry spinning.

Fiber spinning was carried out in a small-scale dry spinning machine. It included a reservoir, a gear pump, a spinning pack (spinneret), a drying chamber (1.5 m in height) and a winding bobbin. The spinning conditions are listed in Table I.

Pyrolysis was undertaken with $Ar/5\%H_2$ as the protection gas, flowing at a rate of 50 cm^3/min. The as-spun fibers were placed in a graphite crucible and heated to the required temperature at a ramp rate of 1°C /min. A soaking time of 2 h at the set temperature was used for all the samples.

Carbon content was analyzed by total combustion method (2400 Series II CHNS/O ANALYZER, PERKIN ELMER); silicon by induction coupled plasma-atomic emission spectroscopy (ICP-2070, BAIRD) method. Oxygen was calculated by the difference, assuming no other elements present apart from these three. Fiber strength was tested in a universal testing machine (INSTRON, MODEL 1123). The gauge length was 20 mm. The crosshead speed was 0.5 mm/min. Other material characterization included powder X-ray difffractometry (XRD, Rigaku D/MAX-RC), Fourier-transform-infrared spectrometry (FTIR, Nicolet 730), thermogravimetric analysis under $Ar/5\%H_2$ (STA 409EP, NETSCH) and scanning electron microscopy (XL30 ESEM-TMP).

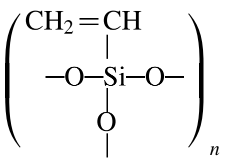
3. Results and discussions

3.1. Optimization of VTMS/H_2O ratios

Preliminary study showed that the VTMS gel produced a silicon oxycarbide phase containing high carbon content after pyrolysis in an inert atmosphere in comparison with the other silicate gels studied, for example, ethyl silicate or tetraethyl orthosilicate gels. This was the primary reason for the selection of VTMS. Because VTMS sol was very difficult to spin into fiber [8], SCA was used in this work as the fiber-forming aid. However, the direct mixing of VTMS, water, SCA and acetone did not give a spinnable dope, because of the inevitable SCA precipitation. It was found that SCA might be compatible with VTMS if VTMS was pre-hydrolyzed before mixing, but the compatibility was strongly dependent on the degree of hydrolysis of VTMS. It was essential to spinning that the hydrolysis product of VTMS did not precipitate in the dope and could remain stable for a long period of time. Phase separation would seriously impair the dope spinnability and fiber quality, such as compositional homogeneity and mechanical properties. The major factor affecting the VTMS hydrolysis was the ratio of water to VTMS. Theoretically 1.5 moles of water is required to fully hydrolyze every mole of VTMS into polysilsesquioxane, as indicated by the reaction below [9–10]:

$$2CH_2{=}CHSi(OCH_3)_3 + 3H_2O = 2[CH_2{=}CHSiO_{1.5}]_n + 6CH_3OH \qquad (1)$$

where $[CH_2{=}CHSiO_{1.5}]_n$ is a polymer with a structure shown below:



$$\left(\begin{array}{c} CH_2{=}CH \\ | \\ -O-Si-O- \\ | \\ O \\ | \end{array} \right)_n$$

In reality, the equilibrium is rarely reached, and the degree of hydrolysis is a function of hydrolysis conditions, such as temperature, time and catalyst.

To determine the optimum amount of water for attaining a VTMS sol suitable for fiber formation, H_2O/VTMS ratios of 2, 3 and 4 were prepared with the acetone/VTMS molar ratio fixed at 6.5 and other parameters constant. For all three compositions a clear solution was obtained after mixing the VTMS, H_2O and acetone. However, on evaporation of the acetone at 50°C, the differences between the three preparations became recognizable. At H_2O/VTMS=4, the originally colorless solution became turbid and rapidly gelled well before the acetone evaporation was complete. The gel yield was ∼94% on the basis of the above overall hydrolysis equation and was calculated using the following expression:

$$\text{Gel yield} = \frac{\text{Gel weight after drying at } 50^\circ\text{C to constant weight}}{\text{Theoretical gel weight}} \times 100\%$$

At H_2O/VTMS = 2, the liquid remained transparent after the acetone removal. Gelation did not take place until some of the un-reacted VTMS was evaporated at

140°C (the boiling point of VTMS is 123°C). The gel yield was much lower, 62%, which was undesirable for fiber production. It was also found that when an SCA solution in acetone [VTMS:SCA = (2.25–4.5):1 by mass] was added into such a mixture, the solution obtained had low viscosity, unsuitable for fiber spinning since the un-reacted VTMS reduced the viscosity considerably. Attempts to concentrate the solution by heating resulted in the precipitation of SCA.

At H_2O/VTMS = 3, gelation was observed ~30 min after the acetone removal at 50°C. This ratio also gave a high gel yield, 90%. More importantly, when the concentrated sol was mixed with SCA/acetone solution, the resultant fluid remained stable for weeks without any phase separation. These results indicated that H_2O/VTMS = 3 was most suitable for the preparation of the spinning dope.

3.2. Optimization of dope compositions

VTMS was capable of producing a hydrolyzed sol with a suitable viscosity for spinning and a good gel yield at H_2O/VTMS = 3. However, the attempts to dry spin such a sol were unsuccessful because of the difficulty in solidifying the newly extruded filaments by heating or chemical reactions after they left the spinneret. FTIR analysis showed that the hydrolysis was not complete. The un-reacted VTMS was difficult to evaporate owing to its high boiling point.

SCA is a readily available polymer with a good fiber-forming ability. It has a common solvent with VTMS, namely acetone. Screening experiments on many different polymers showed that SCA/acetone solutions could tolerate large quantity of VTMS sol without SCA precipitation. Moreover, upon pyrolysis in an inert atmosphere it left no other elements than residual carbon. Elemental analysis showed that the residue contained 99.6% carbon. In other words, the addition of SCA would not introduce impurity into the fiber.

In this work, a SCA/VTMS ratio of 1/2.1 was employed to prepare the spinning dope. Spinnability was the major factor for the selection of this ratio. More SCA would lead to higher residual free carbon, which was detrimental to fiber oxidation resistance, while less SCA made the spinning more difficult. The VTMS sol was mixed with 15% SCA in acetone solution, and the resultant liquid was concentrated to give a spinnable dope. The final dope compositions were 21.2% VTMS gel, 10.3% SCA and 68.5% acetone by mass.

3.3. Pyrolysis

Fig. 1 shows the TGA curves of the VTMS gel, SCA and the fibers. The weight loss of the VTMS gel was gradual, reaching to a constant level ~8% at 800°C. This decrease was due to the evolution of gaseous species during the decomposition of the gel [10]. As the result, an inorganic network was formed with —C—Si—O— linkages as confirmed later by XRD and FTIR analysis. The hydrogen in the gel polymer was released probably as hydrogen gas or small hydrocarbon molecules, for example methane.

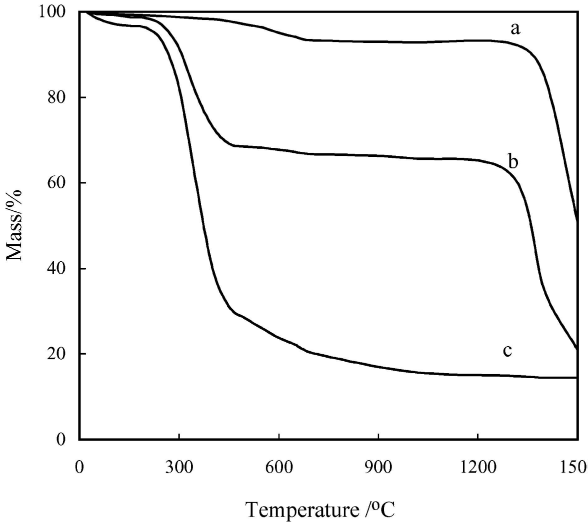


Figure 1 TGA curves of the (a) VTMS gel, (b) fibers and (c) SCA.

No further significant weight change occurred up to ~1300°C, when then a marked reduction took place. Below 1300°C, the pyrolysis product was lustrous black, while above 1300°C a small amount of grayish whiskers were seen. The whiskers were identified as silicon carbide by TEM. As stated previously, the pyrolysis product of the gel was actually an inorganic network containing —C—Si—O— linkages. However, in order to explain the decomposition of silicon oxycarbide phase at elevated temperature, it was usually assumed to be a mixture of SiC, SiO_2 and free C [10].

$$SiO_2 + C = SiO + CO \tag{2}$$

$$SiO + 2C = SiC + CO \tag{3}$$

The gaseous SiO and CO was responsible for the sharp weight loss and the SiC whisker formation.

The decomposition of SCA took place mainly between 200–400°C. A 14.6% residual carbon yield was recorded at 1200°C and in Ar/5%H_2. Calculation showed that the TGA curve of the fibers was essentially the superposition of the VTMS gel and SCA curves. The ceramic yield of the fibers was 65.2% at 1000°C.

The XRD analysis (Fig. 2) is consistent with the TGA results. Below 1300°C, the product was essentially amorphous. The diffraction peaks corresponding to cubic silicon carbide (β-SiC) phase were identified at 1400°C, although the strong background indicated that the material was still predominantly amorphous.

Fig. 3 shows the FTIR spectra of the fiber as a function of pyrolysis temperature. For the as-prepared fiber, the absorptions at 1753 and 1670 cm^{-1} are the characteristic vibrations of —$OCOCH_3$ from the SCA and C=C from VTMS gel. All the C—H absorptions (971, 1012 and 1424 cm^{-1}) disappeared at 800°C, suggesting that the fibers have turned into inorganic materials. However, the absorption at 795 cm^{-1} was still visible, which was attributed to Si—C bonds from VTMS gel. This confirms that the pyrolysed fibers are structured as a silicon oxycarbide phase rather than a mixture of silicon oxide and carbon. At 1400°C, the band at 810 cm^{-1} became conspicuous, corresponding to cubic

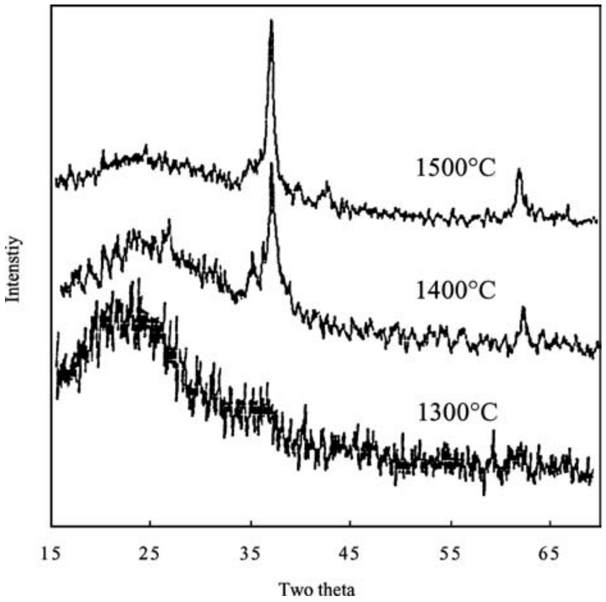


Figure 2 XRD profiles of the fiber after pyrolysis at different temperatures.

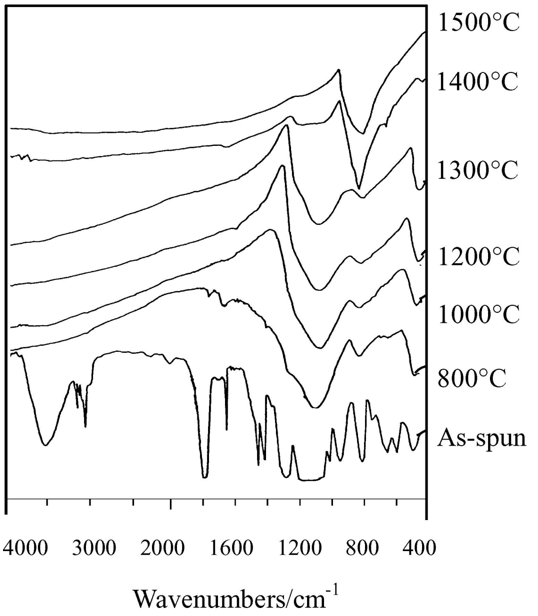


Figure 3 FTIR spectra of the fiber after pyrolysis at different temperatures.

silicon carbide formation [11], at the expense of the Si—O absorption at ~1100 cm^{-1}.

The chemical compositions of the VTMS gel and fibers are listed in Table II as a function of the pyrolysis temperature.

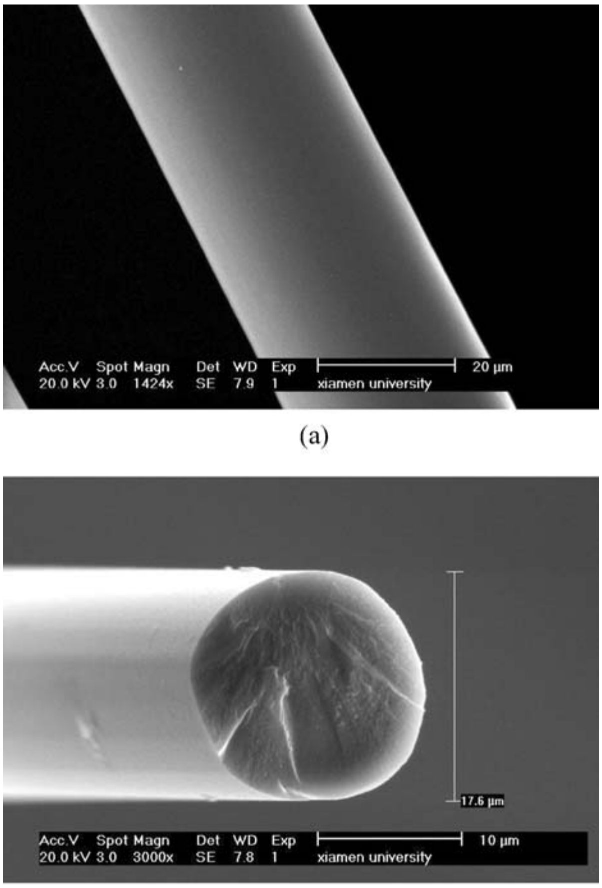
From 800 to 1300°C, the compositional variation with temperature was insignificant. The materials were believed to exist as silicon oxycarbide phase from the VTMS gel plus a small amount of free carbon from SCA decomposition (~5%). At 1000°C the fibers contained a high percentage of carbon 33.2%. The high carbon phase might be useful, for example, to regulate the interfacial bonding with matrix if the fibers are used as composite reinforcements. The oxygen content dropped dramatically at 1400°C, consistent with the formation of silicon carbide by carbothermal reduction.

TABLE II Elemental analysis data (% by mass)

Sample	Temperature (°C)	Si[a]	C[b]	O
VTMS gel	1000	40.3	27.6	32.1
	1300	40.3	28.1	31.6
	1400	53.1	28.1	18.8
Fibers	1000	40.2	33.2	26.6
	1300	41.3	32.8	25.9
	1400	50.9	35.3	13.8

[a] The accuracy was ±1.0%.

[b] The accuracy was ±3.0% due to the incomplete combustion of carbon in the oxycarbide phase.



(a)

(b)

Figure 4 SEM photographs of the fibers (a) as-spun and (b) after pyrolysis at 1000°C.

The SEM photographs of the fibers are shown in Fig. 4. The average diameter of the as-spun fibers was ~20 μm. They had a very smooth surface and brittle fracture cross-section. There was no significant change in fiber morphology below 1300°C, when a small amount of whiskers was occasionally observed on the fiber surface. TEM analysis indicated that these whiskers were silicon carbide. At the same time, surface pitting also occurred and the number density of the pits increased with temperature and soaking duration. The silicon carbide whisker and surface pitting were also the result of the carbothermal reduction between the internal silica and carbon as shown by Equations 2 and 3.

The tensile strength and Young's modulus of the fibers were tabulated in Table III. The strength and elastic modulus of the fibers increased with pyrolysis

TABLE III Tensile strength and Young's modulus of the fibers

Temperature (°C)	Tensile strength (MPa)	Young's modulus (GPa)	Fracture strain (%)
As-spun	184.1	3.6	4.5
800	829.6	55.2	1.5
1000	940.0	63.2	1.3
1100	346.7	33.8	1.3
1200	230.5	28.6	1.4
1300	184.6	20.3	1.1

temperature and reached a maximum at ∼1000°C. Higher temperature resulted in degradation in these properties. The silicon oxycarbide fibers had a lower elastic modulus than glass fibers (typically ∼90 GPa). The strength decrease above 1000°C is attributed to carbothermal reduction inside the fibers, which liberates gaseous silicon monoxide and carbon monoxide, rendering the fibers porous [10]. Similar phenomenon was also reported in polymer-derived silicon carbide fibers (Nicalon)[12]. In other words, the silicon oxycarbide fibers were limited to service temperature below 1000°C.

4. Conclusions

Silicon oxycarbide fibers have been prepared from vinyl trimethoxysilane (VTMS) by a modified sol-gel method and with secondary cellulose acetate (SCA) as the fiber-forming aid. The effect of the pre-hydrolysis of VTMS on the dope spinnability was studied. At H_2O/VTMS = 4, the resultant sol transforms into gel very quickly, unsuitable to obtain a spinnable dope; at H_2O/VTMS = 2, too much un-reacted VTMS exists in the sol, making the extruded fiber difficult to solidify; at H_2O/VTMS = 3, a dope with good spinnability, stability and high ceramic yield is obtainable. Pyrolysis above 800°C converted the fibers into silicon oxycarbide fibers. The fibers pyrolysed at 1000°C in argon had the maximum tensile strength (940.0 MPa), moderate Young's modulus (63.2 GPa) and high carbon content (33.2%). At higher temperature, strength decreased because of the carbothermal reduction of silicon oxide by carbon.

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