Silicon Carbide Fibers from Copolymers of Commercial Polycarbosilane and Silazane

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Abstract: A new approach to prepare silicon carbide fibers by a non-oxidative chemical crosslinking of a commercial, low molecular weight polycarbosilane via copolymerization with vinyl silazane monomer was investigated. Dicumyl peroxide was used as an initiator for copolymerization reactions. SiC fibers were produced by pyrolyzing the spun polymer fibers at 1000°C without any additional curing process. The ceramic yield upon pyrolysis was 65-70%. According to neutron activation analysis, the oxygen content of our copolymer-derived SiC fibers was less than 3 wt%. The tensile strength of our SiC fibers increased slightly after 1400°C heat-treatment while it dropped greatly after 1500°C treatment.

1. Introduction

SiC fibers have been extensively studied for high temperature applications because of several advantages such as high tensile strength, high elastic modulus, excellent thermal shock resistance, good thermal and chemical degradation resistance, low thermal expansion, and high thermal conductivity[1]. Since the invention of Yajima et al.[2], the polymer precursor technology based on polycarbosilane (PCS) has been the most widely used route to fabricate continuous SiC fibers. Their invention gave birth to the commercial NicalonR SiC fibers.

The PCS was first synthesized from polymethylsilane via thermolysis reaction at high pressure[2], which is closely associated with the commercial PCS, X9-6348. The old-type NicalonR ('Old-Nicalon') fibers are produced from the X9-6348. Due to the low molecular weight (MW) of this PCS, reported as 1420-1450[3], a curing process was necessary prior to pyrolysis. The curing is known to be performed oxidatively at 200°C in the air. It was reported that a blending of the PCS with polyvinylsilane at 10 wt% level lowered the curing temperature, accompanied with a slightly increased ceramic yield upon pyrolysis[4]. In both cases, the oxidative curing of spun fibers led to high oxygen contents (10-20 wt%) in Old-Nicalon fibers[5], which is closely related to their low thermo-mechanical stability over 1200°C.

Recently, e-beam curing of low MW PCS fibers has been reported[6-7]. E-beam curing process is known to be used for Hi-Nicalon fibers[8]. In those articles, it was reported that Hi-Nicalon fibers retain their tensile strength significantly up to 1600°C treatments. On the other hand, it was presented that the e-beam curing of spun PCS fibers lasted for several hours[8]. A single-step pyrolysis of X9-6348 PCS using 25-W CW CO₂ laser has been studied[9]. Several problems such as shrinkage, porosity, and cracking, were described[9].

The mechanical and microstructural behavior of Old-Nicalon fibers has been studied extensively.[10-14] Tensile strength of Old-Nicalon fibers was measured after heating to 1400°C in H₂ or in the air[13]. The degree of the thermal degradation was strongly related to the structure of newly forming SiO₂ (whether active or passive form). Over 1400°C, a porous oxide layer formed, which supposedly caused a crack initiation. It was suggested that the thermochemical stability of SiC materials can be greatly improved when the evolution of CO is
restricted [13].

An approach by Toreki et al. using PCS of high MW (5000-10000) to fabricate SiC fibers with low oxygen content was very successful [5, 15]. The high MW PCS with a branched chain structure tends to crosslink rather than melt upon heating. PCS fibers were solution-spun since their high MW PCS is not melting, but is soluble in many organic solvents. Polysilazane, derived from vinyl silazane monomers [16], was added to PCS solution as a crosslinking aid. The oxygen content of the resulting SiC fibers was reported to be less than 2 wt% [5]. The vinyl silazane monomer was considered as a potential crosslinking aid for PCS. In this study, it was examined if a vinyl silazane monomer can be incorporated into the low MW PCS to improve the insusibility of spun polymer fibers.

2. Experimental

The X9-6348 PCS (MW=1420-1450; purchased from Dow Corning Corp.) was copolymerized with a silazane (1,3,5,7-tetramethyl-1,3,5,7-tetraethylcyclotetrasilazane; Hils America T-2000). Dicumyl peroxide (DCP; Aldrich) was used as an initiator. Those three ingredients were dissolved in toluene for a solution copolymerization reaction. The reaction was performed in an acid digestion bomb (Fisher Scientific 01-023) at 130°C for 18 hours. The reaction condition was determined by the previous study of polysilazanes [16].

Two variables were taken into consideration in the copolymerization studies; the ratio of PCS to silazane and the amount of DCP. Fig. 1 illustrates the composition diagram of PCS-silazane copolymerization. The copolymerization reaction gave products in various forms depending on the composition: thin liquid, viscous liquid, liquid-gel mixture, soft gel and hard gel. There was a linear boundary between the non-gelling region and the gelation region. Copolymerization products that formed highly viscous liquids tended to gel easily after one day storage in vials, probably due to air-induced oxidative crosslinking. Copolymerization products obtained in liquids, thin or viscous, were processed further to make fibers.

After being mixed for 30 minutes with a magnetic stirrer, the copolymer solutions were filtered using 0.45 μm PTFE filters (Nalgene 199-2045). The viscosity of the filtered solutions was adjusted to be suitable for fiber spinning using a rotary-evaporator (Brinkmann Rotavap). The viscosity of a copolymer dope was typically 25 Pa·s at a shear rate of 40 s⁻¹, measured at 25°C by a cone-plate viscometer (model HRT).

The copolymer dope was extruded through an eight hole, a 80 (m diameter/hole spinneret, assisted by nitrogen of 50-100 psi. The winding speed of the spun fibers was typically 100 cm/s and the distance between spinneret and spool was 35 cm. Therefore, a typical time for solvent drying from fibers was about 0.3 second. The diameter of the spool was 11.5 cm. The spinning usually lasts 2-5 minutes (fiber length = 120-300 m) without breaking. The spooled spun fibers were cut at three locations, therefore, the typical length of spun fibers prior to pyrolysis was about 12 cm.

The spun fibers were stored in a desiccator under vacuum until they were pyrolyzed. Pyrolysis of spun fibers was performed at 1000°C in a tube furnace (Lindberg GS) using alumina boats (Fisher Scientific 07-680D) under a nitrogen flow (20 scm). Selected pyrolyzed fibers were subsequently heat-treated at elevated temperatures under an argon flow (20 scm). Temperature profiles for the pyrolysis and the heat-treatments at 1300-1500°C were as follows:

- 1000°C pyrolysis: 30°C→(2h)→150°C→(2h)→1000°C (1h hold)→(5h)→30°C
- 1300°C treatment: 30°C→(1h)→100°C→(2h)→1000°C→(1.5h)→1300°C→(1h hold)→(4.5h)→30°C
- 1400°C treatment: 30°C→(1h)→100°C→(2h)→1000°C→(2h)→1400°C→(1h hold)→(5h)→30°C
- 1500°C treatment: 30°C→(1h)→100°C→(2h)→1000°C→(2.5h)→1500°C→(1h hold)→(5.5h)→30°C

SiC fibers were characterized via scanning electron microscopy (SEM; JEOL JSM-6400), x-ray
diffractometer (XRD; Philips APD-3720), scanning Auger microscopy (SAM; Perkin-Elmer PHI-660). XRD spectra were obtained for finely ground powder specimens of fiber batches. SAM spectra were obtained for the central region of a fiber cross-section. Tensile properties were measured in accordance with ASTM D3379-75[17] using Instron® (model 1123). The crosshead speed was 0.02 inch per minute. The gauge length was one inch. A detailed procedure concerning the specimen preparation is found elsewhere[18]. Twenty to twenty-five fiber specimens were tested for each set of data. An epoxy adhesive (Duro Master Mend) was used to glue the fibers on paper mounts. The elemental compositions of our SiC fibers were determined via neutron activation analysis (NAA) [19] performed at the University of Kentucky.

3. Results and Discussion

Table 1 summarizes the fiber processing results with respect to the composition. The insufficiency of spun fibers was dependent upon the copolymer composition. The shadowed region in the table represents copolymer compositions which gave black and easily separable SiC fibers. The other compositions led to the partial melting of spun fibers during pyrolysis, which resulted in curly or non-separable fibers. The melting of fibers during pyrolysis was accompanied by a low ceramic yield compared to non-melting compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>PCS (wt%)</th>
<th>silazane (wt%)</th>
<th>DCP1 (wt%)</th>
<th>DCP2 (wt%)</th>
<th>Ceramic yield (%)</th>
</tr>
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<td>78.5</td>
<td>19.7</td>
<td>1.7</td>
<td>1.7</td>
<td>71.5</td>
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<td>80.1</td>
<td>16.6</td>
<td>1.8</td>
<td>1.5</td>
<td>69.5</td>
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<td>82.8</td>
<td>13.8</td>
<td>1.8</td>
<td>1.6</td>
<td>n.a.</td>
<td></td>
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<tr>
<td>86.8</td>
<td>9.6</td>
<td>1.9</td>
<td>1.6</td>
<td>68.1</td>
<td></td>
</tr>
<tr>
<td>89.2</td>
<td>6</td>
<td>2.0</td>
<td>2.8</td>
<td>66.7</td>
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<td>90.3</td>
<td>6</td>
<td>2.0</td>
<td>1.7</td>
<td>n.a.</td>
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<tr>
<td>91.2</td>
<td>6.1</td>
<td>1.0</td>
<td>1.7</td>
<td>n.a.</td>
<td></td>
</tr>
<tr>
<td>90.2</td>
<td>6</td>
<td>1.0</td>
<td>2.8</td>
<td>n.a.</td>
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</tr>
<tr>
<td>91.2</td>
<td>4</td>
<td>2.0</td>
<td>2.8</td>
<td>n.a.</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Fiber Processing Results versus Compositions

a: dicumylperoxide added for the copolymerization

b: dicumylperoxide added after the copolymerization

For a determination of the optimal silazane content in copolymers, three aspects should be addressed, the spinning behavior, the pyrolysis behavior and the thermomechanical stability at elevated temperatures. The spinning behavior with respect to the composition was not examined in this work. In the light of the pyrolysis behavior, as shown in Table 1, an increase in the silazane content resulted in a slight increase in the ceramic yield of spun fibers upon pyrolysis as well as a better shape of SiC fibers. Concerning the thermomechanical stability aspect, the trend would be reverse. The silazane molecules were incorporated into PCS chains via copolymerization, then were converted into ceramic structures of Si₃N₄ during pyrolysis. The amorphpous Si₃N₄ would be converted into Si₃N₄ₓ the most preferred crystalline structure, upon heat-treatments at elevated temperatures. Since the thermostability of Si₃N₄ is substantially poorer than that of SiC, the silazane content should be desirable at the minimum.

Table 1 indicated that the silazane content in copolymers needs to be greater than 6-10 wt% to avoid melting during pyrolysis. In our work, DCP was added on two occasions. As mentioned previously, DCP was used for copolymerization. DCP was added later again to the copolymerization products to evaluate its effectiveness for the further cross-linking of copolymer fibers. DCP added for copolymerization is referred to as ‘DCP1’ while DCP added later to copolymerization products is referred to as ‘DCP2’ in Table 1. It was found that DCP2 enhanced the insufficiency of spun polymer fibers as well. At 6 wt% of silazane, a copolymer mixed with DCP2 of 2.8 wt% did not melt during pyrolysis while that with DCP2 of 1.7 wt% melted. When the silazane content was less than 6 wt%, however, no good pyrolyzed fibers were produced even with the increased DCP2 content.

It was examined if either DCP or silazane monomer alone could provide the low MW PCS with insufficiency enough for the SiC fiber fabrication. The gelation did not take place when either mixtures of PCS and silazane without DCP or mixtures of PCS and DCP without silazane were heated (18 hours at 130°C) for reaction. Spin fibers derived from above mixtures melted during the 1000°C pyrolysis. Therefore, the crosslinking capability of copolymer fibers was acquired when DCP and silazane were combined together.

According to NAA analysis, the oxygen contents were 2.67(0.05 wt%) while the silicon contents were 61.5(0.7 wt%). These values are obtained based on two measurements. Other elements were not analyzed for due to the high cost. Instead, SAM analysis was employed to determine the approximate elemental compositions of nitrogen and carbon. The oxygen content in our SiC fibers was much lower than that
of Old-Nicalon fibers (10-20 wt%) [15]. This indicates that our copolymerization approach using a silazane monomer can produce SiC fibers with a low oxygen content. The oxygen in our SiC fibers was probably introduced through two sources. The first one was DCP. Considering that the oxygen content in DCP itself is 11.8 wt%, the theoretical oxygen content attributed to DCP should be lower than 0.5 wt%. The second source was probably the oxidation of spun polymeric fibers. During the spinning and the handling, spun fibers were exposed to oxygen in the air. It was empirically demonstrated that the oxygen content in SiC fibers can be reduced by more than one wt% by performing the spinning and the handling of spun fibers under inert atmosphere [18].

Table 2 summarizes averaged tensile properties of our SiC fibers. Batch-to-batch average diameter of pyrolyzed SiC fibers ranged from 14 to 24 (m). Tensile strength (1.0-1.4 GPa) and elastic modulus (114-163 GPa) of pyrolyzed SiC fibers were not high, compared to those (2.5 GPa and 180 GPa, respectively) of Old-Nicalon fibers (~14 μm). This was partly due to the rather large diameter of our fibers. It was observed that tensile strength and elastic modulus of polymer-derived SiC fibers are inversely proportional to their diameter. [18] Interestingly enough, the tensile strengths and the elastic moduli of our SiC fibers increased greatly after 1400°C heat-treatment. After 1500°C treatment, SiC fibers became extremely fragile. A further study is needed for more comprehensive explanation.

Table 2. Tensile Property Ranges of SiC Fibers

<table>
<thead>
<tr>
<th>Fiber treatment temperature (°C)</th>
<th>Range of average fiber diameters (μm)</th>
<th>Range of average tensile strengths (GPa)</th>
<th>Range of average elastic modulus (GPa)</th>
<th>Range of average rupture strains (10^-3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>14-24</td>
<td>1.0-1.4</td>
<td>114-163</td>
<td>6.5-11.7</td>
</tr>
<tr>
<td>1300</td>
<td>19-20</td>
<td>1.1-1.3</td>
<td>154-174</td>
<td>7.2-7.6</td>
</tr>
<tr>
<td>1400</td>
<td>20-23</td>
<td>1.2-2.1</td>
<td>160-203</td>
<td>5.7-12.5</td>
</tr>
<tr>
<td>1500</td>
<td>19-23</td>
<td>0.4-0.5</td>
<td>169-203</td>
<td>2.0-4.2</td>
</tr>
</tbody>
</table>

Fig. 2. Tensile strength retention comparison between Old-Nicalon and our SiC fibers.

The Old-Nicalon fibers are known to degrade substantially after 1200°C treatments [13]. Fig. 2 compares our SiC fiber with Old-Nicalon fibers in terms of tensile strength after treatments at elevated temperatures. The strength retention for the y-axis in the plot is defined as the ratio of fiber tensile strength after each treatment to that after a 1000°C pyrolysis. The tensile strength of Old-Nicalon fibers are substantially diminished after heat-treatments over 1200°C. The strength retention of our SiC fibers after 1300°C treatment was about 0.9 and that after 1400°C treatment was even greater than one. The strength retention of our SiC fibers fell to 0.4 when they were heat-treated at 1500°C.

Fig. 3 shows SEM micrographs of our SiC fiber surfaces after heat-treatments at 1300-1500°C. Compared to the smooth surfaces of spun polymer fibers, our SiC fibers after pyrolysis had some roughness of a few tenths of microns in size. Catastrophic fractures of brittle ceramic fibers are usually caused by a crack propagation initiated from their surface defects. Therefore, the relatively
low strength of our pyrolyzed SiC fibers was
resulted not only from their large diameters, but
also from their rough surfaces. The fiber surface
after a 1400°C treatment appeared to be even
smoother and denser than that of pyrolyzed fibers,
which can explain partly how the strength retention
of 1400°C-treated SiC fibers became greater than
one. After a 1500°C treatment, our SiC fibers had a
porous layer on the surface. The porous layer was
formed probably due to the formation of gaseous
products by the following reaction:

\[ \text{SiC} + \text{O}_2 \rightarrow \text{SiO} \uparrow + \text{CO/CO}_2 \uparrow \]

The thickness of the porous layer was about one
micron, measured from the SEM analysis of fiber
cross-sections.

As mentioned previously, SiC fibers with a lower
silazane content were expected to have a greater
thermomechanical stability than those with a higher
silazane content. Examination of SEM micrographs
and tensile properties of SiC fibers after 1300-1500°C
heat-treatments did not reveal a significant effect of
silazane content. The actual results correlated in a
reverse trend. The difference, however, was
extremely small. It could be possibly because the
range of silazane content considered in this study
was not sufficiently large.

Fig. 4 illustrates the XRD patterns of our SiC
fibers as the treatment temperature increases. SiC
fibers after 1000°C pyrolysis had only a broad peak
near 2θ = 35.6°. Three peaks of SiC at 2θ = 35.6,
60.0 and 75.5° were enlarged as SiC fibers were
treated at higher temperatures. Those three peaks
corresponded to (-SiC crystalline of (111), (220) and
(222) planes, respectively[20]. The growth of those
peaks resulted from the crystallization of amorphous
Si-C microstructure by thermal activation. As tem-
perature increased, the peak width tended to
decrease, which was primarily associated with the
grain growth of β-SiC crystallites.

Even though the silazane content in the
copolymers was 6-20 wt%, XRD peaks for no other
crystalline phases such as SnS₁₇ than SiC were
detected in our SiC fibers after 1000°C pyrolysis or
1300-1500°C treatments. SAM analysis indicated that
the nitrogen content in our SiC fibers was below a
detectable level. Considering that the theoretical
nitrogen content was no less than 2.5 wt% in spun
polymeric fibers, most of the nitrogen must have
been lost, presumably in the form of HCN, during
pyrolysis. However, it is controversial to the fact
that an increased silazane content tended to result in
a slight increase of ceramic yield of fibers upon
the 1000°C pyrolysis.

![XRD patterns of SiC fibers](image)

**Fig. 4.** XRD patterns of SiC fibers: (a) as-pyrolyzed
at 1000°C and after heat-treatments at (b)
1300°C, (c) 1400°C, and (d) 1500°C.

4. Conclusions

As a novel method to make commercial, low MW
PCS infusible during the 1000°C pyrolysis, a
copolymerization with a vinyl silazane monomer
was investigated. Dicumyl peroxide was used as an
initiator. Results of our work are summarized as
follows:

- Compositions for copolymerization to give
  products suitable for fiber processing were
determined. The minimum silazane content was
6-10 wt% to avoid melting of spun fibers while
the maximum content was about 20 wt% above
which gelation easily occur during the copoly-
merization reaction.

- Our SiC fibers included the oxygen less than 3
  wt%, much lower than that (10-20 wt%) of
Old-Nicalon SiC fibers. The tensile strength of
our SiC fibers slightly increased after 1400°C treat-
ment, along with the densification of fiber
surfaces. After a heat-treatment at 1500°C, however,
tensile properties greatly decreased, attributed to
the development of porous microstructure in
surface layers.

- A further study is necessary not only to produce
SiC fibers of improved properties, but also to
understand more comprehensively.

References

17. "Standard test method for tensile strength and Young's modulus for high-modulus single filament materials", ASTM D 3379-75 (approved 1982), Philadelphia, PA, USA