Silicon Carbide Fibers Derived from Polycarbosilane Doped with Iodine as Oxygen Inducer

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Abstract: Silicon oxycarbides (SiOxCy) fabricated at 1300°C from iodine-doped polycarbosilane (PCS) have been shown to have high tensile strength. Iodine doping of PCS can induce oxygen atoms into the molecular structure of PCS, which forces it to start cross-linking at a relatively low temperature of 180°C. The mechanical properties of fabricated SiC fibers strongly depend on the degree of cross-linking during stabilization. In this study, the role of oxygen in the cross-linking reaction of PCS was investigated by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TG), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) analysis.

Keywords: silicon carbide fiber, oxi-stabilization, iodine doped polycarbosilane, oxygen inducer, cross-linking

1. Introduction

SiC fibers have been used as one of the main components for high-temperature composite materials due to its high-temperature stability up to 1,300°C in air. In the 1970s, Yajima had developed a method to fabricate continuous SiC fiber with melt-spinning from the polymer precursor polycarbosilane (PCS) [1]. Consequently, melt-spun PCS fibers needed to convert from thermoplastic to thermosetting with chemical curing (pre-treatment) for high-temperature pyrolysis. The chemical curing is a crucial process for fabrication of SiC fibers; it prevents softening and melting problems of PCS during the high-temperature pyrolysis. The conversion of thermoplastic polymer into thermosetting is a sensitive process that based on cross-linking of PCS, the linear structure of the thermoplastic polymer is converted into thermosetting polymer due to several reactions such as dehydrogenation and oxidation during the curing [2–5]. This conversion process heavily depends on the molecular weight of PCS caused by its hydrogen compound and volatile contents. In general, it is difficult to form a fiber shape using high molecular weight PCS due to its high softening and melting point. Also, the high molecular weight results in increasing viscosity of PCS, it leads to damage to the continuous fiber during the spinning. However, the spun PCS fiber from the high molecular weight PCS is easily can be converted into thermosetting because of its low hydrogen compound and volatile contents. On the other hand, the low molecular weight PCS results in a lower viscosity of PCS and shows good spinnability. The disadvantage of using the low molecular weight PCS, the fiber shaped PCS can be melted and failed to keep its original shape during the curing and heat treatment process [6]. The conversion mechanism from thermoplastic to thermosetting is carried out by oxygen cross-linkage on PCS immediately after the absorption and diffusion of oxygen into the PCS. The absorption and diffusion of oxygen occur on the surface and interior part of the PCS fiber, those are inducing rapidly on Si-H, C-H, and Si-Si cleavage; it leads to recombine by forming Si-O-Si, Si-C and C=C bonds [7]. Also, during the pyrolysis, the chemical-treated PCS fiber to produce SiO and CO gases, from which Si-C-O and Si-C forms of SiC fibers are
produced. Thus, the chemical curing and the heat treatment processes are critical parts of the organic-inorganic transition for fabrication of SiC fibers. These processes determine the mechanical strength of SiC fibers, based on the amount of oxygen involved in the silicon oxycarbide (SiCxOy), a chemical formation that yields β-SiC crystal at temperatures <1,300 °C. Therefore, the control for absorption and diffusion of oxygen into PCS fiber is critical to fabricating the SiC fiber. Hemida et.al proceeded the experiment that PCS fiber is exposed to ozone in order to analyze penetration degree of oxygen into PCS. However, the cross-linking is progressed heterogeneously in the PCS fiber due to the difference of reaction velocity at surface and core of the PCS fiber [8]. In this study, PCS was blended with various concentration of iodine solution, which was used as an oxygen inducer for fabrication of continuous SiC fiber. Through the morphology, crystal structure, chemical composition, and tensile strength of fiber heat-treated in this process, it was confirmed that the iodine in PCS could induce oxygen efficiently into PCS fiber for cross-linking at the low-temperature range.

2. Experimental

Polycarbosilane (TBM Tech. Co. Ltd., Korea) was used as a precursor for fabrication of SiC fibers. The characteristics of the PCS precursor summarized in Table 1. An analytical grade of iodine powder (Daejung Chemical, Korea) was used as the doping element. The fabrication procedures of SiC fiber have been described as schematic diagram in Figure 1.

Toluene used as a solvent to dissolve PCS and iodine, and each of their solutions was prepared separately. The iodine solution concentration was 0.3, 0.5 and 1.0 wt.% of the amount of PCS weight, respectively. Subsequently, the mixture of PCS and iodine solution was dried on a hot plate at 80–100 °C, while stirred with the speed of 85 rpm for 8 hrs. The toluene was evaporated after the reaction between PCS and iodine in the mixture. The molecular weight of PCS was determined by gel permeation chromatography system equipped with Waters 515 HPLC pump, a Waters 2414 refractive index detector. Chemical structure of iodine doped PCS was determined by Fourier transform infrared spectroscopy (FT-IR) analysis equipment (FT/IR-4100, JASCO, Japan). Thermogravimetric analysis has been employed to determine the carbonization behavior of the iodine doped PCS up to 1,000 °C with 10 °C/min of the heating rate under nitrogen flow with 20 ml/min of flowing (DTG-60H, Shimadzu, Japan). The iodine doped PCS powder was melted and spun with single-hole spinneret spinning machine for fabrication of PCS fiber. And then, the melt-spun PCS fibers were stabilized at 120 °C, 160 °C, 180 °C and 200 °C in the curing chamber with an air atmosphere. Subsequently, all the stabilized PCS fibers were heat-treated at 1,300 °C with the heating rate of 10 °C/min for 2 hours in an argon atmosphere. SEM analysis was used for the surface and cross-sectional imaging analysis of the fabricated SiC fibers. Also, EDS analysis was performed for the elemental analysis (Si, C, O, I) of fabricated SiC fibers. Tensile strength measurement proceeded with 30 mm length of fibers with 0.5 mm/min speed of extension.

3. Results and Discussion

Figure 2 indicates FT-IR spectrum of as-received and iodine doped PCS, it shows the typical stretches of PCS at 2,900 cm⁻¹ (C-H), 2,100 cm⁻¹ (Si-H), 1,250 cm⁻¹ (Si-CH₃) and 1,000 cm⁻¹ (Si-CH₂) [9]. Also, there are no differences observed in the intensity of peaks as according to iodine content (wt.%). It confirmed that the iodine was doped successfully into PCS without influence for molecular weight and chemical structure of PCS. Otherwise, the cross-linking reaction between PCS and iodine was not occurred at this stage of the experiment, and it proved by unchanged stretchings such as Si-H and C-H in the PCS. The possible cross-linking can be affected some negative ways on the

| Table 1. Properties of polycarbosilane (PCS) as the raw material for SiC fibers |
|-----------------|-----|-----|------|------|-----|
| Content        | S.P.(°C) | M.P(°C) | Mw(Dalton) | Mn(Dalton) | P.D. |
| PCS1602-C      | 148   | 195   | 2480    | 956     | 2.59 | TBM tech. |

Figure 1. Schematic diagram of doping of PCS and fabrication of SiC fibers.
melt-spinning process due to increased viscosity, softening and melting point.

Figure 3 shows FT-IR spectrum of iodine doped PCS, which have oxi-stabilized at 180 °C in air. In order to observe changes of chemical bonds, peak intensities were compared between as-received, before and after stabilization of iodine doped PCS samples. After the oxi-stabilization, an apparent cleavage appeared on the stretching for Si-H at 2,100 cm⁻¹, and cleavage ratio of Si-H (2,100 cm⁻¹) to Si-CH₃ (1,250 cm⁻¹) was increased along with doped iodine content in the PCS. Those cleavages indicate that the oxygen attacked hydrogen chemical bonds easily, which is called “dehydrogenation” and oxygen was diffused efficiently into PCS molecular structure for cross-linking. Also, new stretchings such as Si-OH, C=O and C=C have emerged at 3,250–3,750 cm⁻¹, 1,500–1,750 cm⁻¹ in oxi-stabilized PCS [10]. Those resulted from the cross-linking reaction between oxygen and hydrogen chemical bonds. The peak intensities for C=C, C=O, Si-OH stretchings became stronger in proportion to contents of iodine which was used as oxygen inducer into PCS fiber. Hence, it is considered that the iodine doped low molecular PCS can be utilized for further fabrication of continuous SiC fiber.

Figure 4 shows thermogravimetric curves of PCS fibers according to doping content with the iodine. The ceramic yield of as-received, 0.3%, 0.5% and 1.0% iodine doped PCSs were 74.48%, 83.340%, 85.57% and 87.02%, respectively. Otherwise, the ceramic yield of iodine doped PCS tended to improve along with doped iodine content within the PCS. Results mentioned above of iodine doped, unstabilized PCS (Figure 2), there were no changes appeared in the chemical bonds. On the other hand, the oxi-stabilization process forced to induce oxygen into PCS and then, the induced oxygen attacked hydrogen chemical bonds for cross-linking in low molecular PCS. Earlier literature suggested the oxi-stabilization of PCS fiber was conducted around 300 °C in the air because of oxygen can diffuse into PCS at that temperature. The presence of iodine into PCS can accelerate the oxi-stabilization of PCS fiber at a relatively low temperature at 180 °C. The increased ceramic yield of iodine doped, oxi-stabilized PCS indicates that iodine doping into PCS leads better cross-linking reaction, which is started by induced oxygen into PCS.

Figure 5, 6 and 7 show SEM images of SiC fibers, those were oxi-stabilized at 160 °C, 180 °C and 200 °C, respectively. As-received PCS fiber failed to keep the fibrous shape and melted during the pyrolysis at 1,300 °C. In contrast, iodine doped PCS fiber could keep fibrous shape without any softening during the pyrolysis; even oxi-stabilization proceeded at 160 °C. It shows that iodine doping has an excellent effect for inducing oxygen for cross-linking.

Figure 8 shows cross-section images and EDS data of PCS and SiC fiber as according to iodine doping after oxi-stabilization and pyrolysis. Cross-sections of SiC fiber have shown smooth microstructure after the oxi-stabilization and pyrolysis. Also, the content of carbon (C), silicon (Si), oxygen (O) and iodine (I) in the PCS fiber were determined 61 wt%, 25 wt%, 13 wt% and 0.08 wt%, respectively (Figure 8(a)). After the pyrolysis, the amount of carbon and oxygen were increased slightly, while decreased amount of silicon and iodine in the pyrolized SiC fiber (Figure 8(b)).
Figure 5. SEM images of fabricated SiC fibers from oxi-stabilized PCS at 160°C.

Figure 6. SEM images of fabricated SiC fibers from oxi-stabilized PCS at 180°C.
Figure 7. SEM images of fabricated SiC fibers from oxi-stabilized PCS at 200 °C.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>C (wt%)</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
<th>I (wt%)</th>
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<td>Min</td>
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Figure 8. Cross-sectional images and energy-dispersive spectroscopy (EDS) data of iodine-doped PCS fibers after oxi-stabilization (a) and of SiC fibers from iodine-doped PCS after pyrolysis (b).

<table>
<thead>
<tr>
<th>Statistics</th>
<th>C (wt%)</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
<th>I (wt%)</th>
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The presence of 0.5% iodine. The ceramic yield of iodine doped PCS fiber at 2.1 GPa, which have oxi-stabilized at 180 °C with the presence of 0.5% iodine. The ceramic yield of iodine doped PCS tended to improve along with increased iodine content within the PCS. The presence of iodine into PCS can accelerate the oxi-stabilization of PCS fiber at a relatively low temperature at 180 °C. The increased ceramic yield of iodine doped, oxi-stabilized PCS indicates that iodine doping into PCS leads better cross-linking reaction, which is started by induced oxygen into PCS.

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