Influence of pyrolyzed temperature on the formation of silicon carbide fiber from polycarbosilane in electrospinning method

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Abstract. The synthesis of silicon carbide (SiC) fibers by electrospinning method was done using polycarbosilane (PCS) as precursor and dimethylformamide (DMF)/toluene as solvent. Knowing the heat treatment of fibers consist of curing and pyrolysis, there were two steps in the major reaction. The curing process is by heating in air to make an oxidative cross-linking of the PCS. The pyrolysis process causes chemical decomposition from organic to inorganic compounds. These composition changes were described through Fourier Transform Infrared FTIR, Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS) analysis. The products of electrospinning and curing were characterized by FTIR and TGA. The conversion to ceramic of PCS under various pyrolysis temperatures (1200, 1300, 1400, 1500) °C has been investigated and the products of this process were characterized by FTIR and XRD. Elemental analysis of the fiber as received and after cured showed that the ratio of H and C to Si decreased with holding time at the cure-temperature while the amount of oxygen increased. Meanwhile, the pyrolyzed generally produced silicon oxycarbide SiOxC. Crystalline SiC β-SiC was found at temperature 1500 °C.

Keywords: SiC fibers, polycarbosilane, electrospinning, curing, pyrolysis

1. Introduction

Silicon carbide (SiC) is known as one of highly significant semiconductor substances generated through the covalent bond amongst Si and C. This substance is a perfect preference for the applications where tough environment is involved, such as high-power, high frequency as well as high temperature. PCS conversion into ceramic is normally obtained through a heating process of the polymer precursor to the temperature higher than 1000 °C in inert atmosphere condition. Numbers of stages in SiC fibers were observed to be involved in the PCS pyrolytic conversion and oxidation-cured methods. The SiC fibers derived from the pyrolysis process of polymer carry beneficial properties, namely the flexibility and fine-diameter. Polycarbosilane’s synthesis as precursor, polymer-derived C fibers performed by Yajima et al. [1] has been widely investigated. The said method involves four processes: synthesis, spinning, curing and pyrolysis.

Electrospinning is an exceptional multipurpose system -enables the production of fine-fibers in tiny diameters, from couple of microns to tens of nanometer- by the means of processing or melting the polymeric solution [2]. Electrospinning is a fiber fabrication method using electrical fields to stretch spinnable jets from polymer solutions. It has been used as a versatile technique of fiber fabrication such as polymers and ceramic fibers. The working principle is to conduct electric spinning using an electric field to stretch spinnable jets from polymer solutions.
The synthesis of SiC fibers by electrospinning of PCS solutions is followed by thermal curing and pyrolysis. PCS melts before decomposition. Thus, it cannot be directly heated up to obtain SiC. During crosslinking, oxygen helps to bridge the PCS molecules to form larger ones. The curing process allows PCS to have a more stable structure. The PCS after crosslinking does not melt before decomposition during the subsequent heat treatment in pyrolysis process [3–4].

During the preparation of SiC fibers, in the curing process, oxidation takes place in PCS fibers due to the heat treatment in the air. This heat treatment is intended to provide the infusible article and to maintain its form, as well as to generate a high ceramic results afterward [5]. This stage is a crucial process, since considerable mass of fibers could be lost throughout the pyrolysis process.

As SiC-forming precursor, PCS has been widely utilized by many researchers, in which the process of producing SiC fibers from PCS involves few steps of method, i.e. synthesis, spinning, curing and pyrolysis [1,6].

The temperature’s influence on SiC formation process was studied in this research. The fibers were pyrolyzed at temperature 1200, 1300, 1400 °C and 1500 °C. The fibers were analyzed in order to describe the structural change during the heat treatment. The characterization was done by Fourier Transform Infrared (FTIR), Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS).

2. Experimental
Polycarbosilane (PCS) was utilized as a precursor through dissolution of toluene and N, N-dimethylformamide (DMF) as solvent. PCS at 1.2 g/mL was dissolved with solvent with a composition of 30 % (% DMF/toluene). The solution was gently stirred for 12 hours minimum to make sure the PCS solution is homogeneous. This solution served as feeding solution for electrospinning process. During the electrospinning process, the voltage was set at 17 kV and the tip to collector distance was set at 10 cm. In each process, the feeding solution was set at 2 mL and feed rate at 1 mL/hour. The obtained fibers was cured at 200 °C for 1 h at the rate of 2–3 °C/min. For the conversion of the cured fibers into the SiC fibers, the fibers were pyrolyzed at (1200,1300, 1400 and 1500) °C for 1 h at the rate of 2–3 °C/min.

The characterization of the generated fibers from electrospinning was done with Fourier Transform Infra Red (FTIR). The cured fibers were characterized with FTIR and Thermogravimetric Analyzer (TGA). The pyrolyzed fibers were characterized by FTIR, X-ray Diffraction (XRD) and Energy Dispersive X-ray Spectroscopy (EDS).

3. Results and discussion

In this chapter we discuss the structural changes of PCS, starting from the original form until pyrolysis took place.

3.1. The crosslinking in curing process

The crosslinking behaviors in curing process of PCS fibers will be discussed. PCS melts before decomposition. Thus, it cannot be directly heated up to obtain SiC. During curing process, oxygen helps to bridge the PCS molecules to form the larger ones. The PCS after crosslinking does not melt before decomposition 1. The effect of the temperature and the heat-treatment duration on the crosslinking of the PCS was studied.

The as-received PCS used in this work had three major structural elements, they are: Si-C bonds, Si-CH-Si bonds and SiCH. bonds. The three of them, Si-CH and Si-CH-Si bonds are crucial in consequence of the relation to the oxygen control included during the next curing process. C-H bonds and Si-H bonds are the side groups of PCS. The curing process allowed PCS to have a more stable structure so that they would not melt during the subsequent heat treatment. FTIR spectra for PCS before curing was similar to what Setiawan et al. [7] have done for several DMF concentrations. Comparison of FTIR results for samples of before and after curing, is shown in figure 1 where the absorption peak appears in the sample after curing where Si-H strain (2100 cm⁻¹), Si-CH. (1250 cm⁻¹) and CH (2850 cm⁻¹) represent the Si-CH group.

There is an increase peak of Si-CH-Si (1000 cm⁻¹). There are two peaks that appears on the FTIR graph of curing fiber, Si-O group (470 cm⁻¹) and Si-OH (3200 cm⁻¹) with a very dominant peak, strain CH (1450-1350 cm⁻¹), cluster C = C (1640-1680 cm⁻¹), other than that, there is a CH 2850 cm⁻¹ group. In the curing process there was a condensation reaction between the residual CH groups in the structure, where it was released H. and CH. and formed Si-C-Si bridges with the consequence of increasing
crosslinking network. Si-CH₃, Si-H and C-H groups can react with each other to produce hydrogen and methane gas.

The presence of oxygen during the curing process causes a reaction between oxygen with Si and C groups, causing the decomposition of PCS so that the Si-H group decreases and the Si-O and Si-OH groups increase, indicating the reaction of the oxidation bridge, C=C also appears because of the dehydrogenation or the release of hydrogen. The results of this study indicate that they are not much different from the research of [4, 6, 8–9]. The phenomenon of crosslinking on PCS fibers during the curing with air conditions is described in figure 2.

The influence of the heat-treatment temperatures on the PCS decomposition was observed with TGA, measurements, which was made to a temperature of 1000 °C, with air conditions and a rate of 10 °C / minute of heating. Figure 3 shows the PCS fibers prior to curing at room temperature up to 200 °C. The mass decreased of about 5.7% due to evaporation in the PCS solvent, it was possible to occur due to the release of oligomers with low molar masses and also possible due to the evaporation of water contained in the fibers due to air humidity during storage [10].
The PCS gained was about 5.8 % by weight at temperature ~ 200 °C, and then peaked to 6.3 % at temperature ~ 300 °C. This would be due to the interaction of oxygen with Si, which disintegrated from Si-H bond. So, the addition of 0.5 % weight is due to the entry of oxygen into the PCS structure to form of what called as crosslinking. Then, the weight decreased at temperature ~ 400 °C and furthermore the higher the heating temperature decreased the fiber weight. The weight change curve started to dropping down when the temperature was above 300 °C. This suggests that the early decomposition of the side groups in PCS such as methyl silicone bonds, silicon hydrogen bonds and carbon hydrogen bonds, lost the mass due to hydrogen and low molecular weight hydrocarbons’ lost during the dehydrogenation and dehydrocarbonation condensation reactions. PCS fibers are highly sensitive against oxygen in the heat treatment process in the air, so thermal decomposition in the fibers mainly occurs on the PCS fiber side chain [9]. The curve pattern decreases from 300 °C to 1000 °C has some steep drop point, indicating the decomposition takes place through several stages. There are two parts of steep decrease at ambient temperature 530 °C to 620 °C, then at a temperature of about 855 °C to 920 °C, indicating at the temperature decomposition occurs so much loss of mass.

The TGA results were also supported by FTIR fiber samples prior to curing and after curing as shown in figure 1. There were peaks that appear on the FTIR graph, Si-O (470 cm⁻¹) and Si-OH (3200 cm⁻¹) with a very dominant peak. The oxygen that enters the molecule causes weight increase. When the temperature reached around 260 °C to 300 °C there was no more weight increase. The oxygen during the process reacted with Si and C groups to form Si-O and O-H groups. After the temperature reached 400 °C, the PCS backbone begins to decompose. The Si-C and Si-CH-Si bonds become very weak and at that time it is believed that the breaking of Si-CH₃, Si-H and CH groups decreases, so the PCS weight decreases [4,11–12].

3.2. Pyrolysis

Figure 4 shows the FTIR spectra for SiC fiber that pyrolyzed at different temperatures. The organic parts of PCS were transformed into a more inorganic state during pyrolysis. High weight lost and gaseous evolution of the most of H, and CH, were related with these reactions. Si-H and C-H bonds were immediately broken. FTIR indicates that the major bonds available were Si-CH₃ (1250 cm⁻¹) and Si-CH₂-Si (1020 cm⁻¹) and Si-OH (3400 cm⁻¹). The band that broadening at about 3700 cm⁻¹ probably because of O-H stretching of Si-OH. Along with the temperature increase, C-H bond decreased while the Si-H, and Si-CH bonds disappeared. At the temperature of 1400 °C the connectivity of Si-C-Si bonds increased and a network structure can be formed through condensation reaction amongst CH, and CH units, then, Si-C (820 cm⁻¹) bonds started to appear and also C-O (1200 cm⁻¹) bonds which was caused by chemical decomposition with reaction [4] as follows:

\[ \text{Si(C}_x\text{O}_y \rightarrow \text{SiC}_s + \text{SiO}_g + \text{CO}_g + C_s] \]  

Oxygen was introduced in oxidation cured; the oxygen actually will be lost as SiO gas and CO gas during heating in pyrolysis process. However, CO gas evaporates at temperature no less than 1500 °C, so to remove all oxygen content it needs to be heated to more than 1500 °C. The crystals of SiC were formed when the temperature raised to 1400 ºC or above, it was probably because of the crystal growth of β-SiC [4,13–14]. During the decomposition process, the evolution of H gas and Si-H bond was interrupted and C-H was broken, while Si-C-Si bond increased. During pyrolysis temperature of 1400 °C and 1500 °C the C-O bonds appeared.
Figure 4. FTIR spectra of SiC fibers

Figure 5. XRD spectra of SiC fibers

In the XRD pattern of figure 5, during the pyrolysis at 1400 °C and 1500 °C, the SiC crystals begin to grow, showed by the peak between 30-40 °, indicating the formation of SiC crystals at hkl (111) and a low peak between 60-70 ° which also indicating the SiC (220). The fibers of pyrolysis at 1200 °C and 1300 °C are still amorphous, so there is no peak in the XRD graph. Crystallinity increases with the increasing temperature; crystal growth begins at temperatures above 1300 °C.

It has been described in introduction, that SiC has a varied crystal form (polytypes) XRD data shows only 1500 °C pyrolysis sample fibers and 1400 °C pyrolysis sample fibers from which have a crystal lattice but are still in small amounts, marked by gentle peaks and many noise-like spectra that
The element content in pyrolysis fibers was analyzed using EDS. The results stated that the chemical structure was Si-O-C, with Si:CO ratio shown in Table 1. The oxygen contained in the fibers comes from the curing process because the curing process was carried out under air conditions causing an increase in oxygen content due to oxidation and replacement of Si-CH bonds with Si-O-Si and Si-O-C during cross linking, thereby increasing the percentage of oxygen content. Table 1 shows the phenomenon that by heat treatment during pyrolysis, the oxygen content decreased, it is because during the pyrolysis process there is formation of gas product (SiO and CO) [4, 6, 17, 18].

| Elements | Temperature (°C) |
|----------|------------------|
| Si (%)   | 1200  1300  1400 1500 |
| O (%)    | 27.31  20.78  30.75 41.11 |
| C (%)    | 55.71  35.13  51.63 44.78 |
| Fiber composition | SiO\textsubscript{1-x}C\textsubscript{x} | SiO\textsubscript{1-x}C\textsubscript{x} | SiO\textsubscript{1-x}C\textsubscript{x} | SiO\textsubscript{1-x}C\textsubscript{x} |

indicating many structures of SiC are still in amorphous form. The SiC crystal structure that may grow is β-SiC or 3C-SiC, where the β-SiC crystal structure is formed on the surface of the fiber when the temperature is increased to 1300 °C or higher [4,15–16]. So, only SiC fibers in the pyrolysis at 1400 °C and 1500 °C only appear on the XRD graph, since the SiC fiber phase at temperatures below 1300 °C is still amorphous, when the temperature rises to 1300 °C or greater, SiCO decomposition occurs, and forms SiO gas, SiC crystals and free carbon, then SiC crystal precursors occur because of the reaction between free carbon and SiO gas forms large crystals can be seen on fibers’ surface. SiC crystal formation reaction can be seen in the following equation:

$$\text{SiO}_2(g) + 2\text{C}_2(g) = \text{SiC}_2(g) + 2\text{O}_2(g)$$

3C-SiC is the only polytype with a cubic crystal structure also called β-SiC. 3C-SiC has a sequence of arrangements of a double atomic layer is ABCABC. The “C” in 3C-SiC indicates the cubic crystal structure and ‘3’ represents the amount of layers of two atoms in a loop unit (ABC). A layer of Si (or C) atoms in a stacking order might have a cubic (k) or hexagonal (h) shape, but 3C-SiC only has a type-k atom.

The element content in pyrolysis fibers was analyzed using EDS. The results stated that the chemical structure was Si-O-C, with Si:CO ratio shown in Table 1. The oxygen contained in the fibers comes from the curing process because the curing process was carried out under air conditions causing an increase in oxygen content due to oxidation and replacement of Si-CH bonds with Si-O-Si and Si-O-C during cross linking, thereby increasing the percentage of oxygen content. Table 1 shows the phenomenon that by heat treatment during pyrolysis, the oxygen content decreased, it is because during the pyrolysis process there is formation of gas product (SiO and CO) [4, 6, 17, 18].

4. Conclusions

SiC fibers have been successfully synthesized by electrospinning method with polycarbosilane precursors and DMF / Toluene solvents, followed by heat treatment in curing and pyrolysis processes. The curing process was performed with air condition at temperature of 200 °C. The heat treatment analysis was conducted using TGA which proved that the process of fiber decomposition to ceramic form occurred from about 300 °C. The conversion of organic parts in PCS resulted in a more inorganic state during pyrolysis. High weight lost and gaseous evolution of the most of H, and CH\textsubscript{4} were related with these reactions. Si-H and C-H bonds were immediately broken. The formation of SiC fibers occurred at the pyrolysis stage that is the heat treatment with temperature variation 1200 °C, 1300 °C, 1400 ºC and 1500 °C. SiC fibers obtained showed an amorphous and slightly crystalline phase in pyrolysis fiber of 1400 °C. Crystalline SiC β-SiC was found at temperature 1500 °C with elements composition of SiO\textsubscript{1-x}C\textsubscript{x}.

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