

## Research Article

# Synthesis of $\beta$ -SiC Fine Fibers by the Forcespinning Method with Microwave Irradiation

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A rapid method for synthesizing  $\beta$ -silicon carbide ( $\beta$ -SiC) fine fiber composite has been achieved by combining forcespinning technology with microwave energy processing.  $\beta$ -SiC has applications as composite reinforcements, refractory filtration systems, and other high temperature applications given their properties such as low density, oxidation resistance, thermal stability, and wear resistance. Nonwoven fine fiber mats were prepared through a solution based method using polystyrene (PS) and polycarbomethylsilane (PCMs) as the precursor materials. The fiber spinning was performed under different parameters to obtain high yield, fiber homogeneity, and small diameters. The spinning was carried out under controlled nitrogen environment to control and reduce oxygen content. Characterization was conducted using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The results show high yield, long continuous bead-free nonwoven fine fibers with diameters ranging from 270 nm to 2  $\mu$ m depending on the selected processing parameters. The fine fiber mats show formation of highly crystalline  $\beta$ -SiC fine fiber after microwave irradiation.

## 1. Introduction

In the past 50 years, microwave irradiation has been utilized to process various materials such as semiconductors and inorganic and polymeric materials. More recently, microwave energy has been used to sinter powdered metals as well as ceramic systems [1]. Microwaves are electromagnetic radiation with a wavelength from 1 mm to 1 m with frequencies in the range of 1 to 300 GHz [2]. Most common microwaves furnaces used for industrial and scientific applications operate at a frequency of 2.45 GHz [3]. The most effective way to produce microwaves is from a magnetron source, but they can also be produced from klystrons, power grid tubes, traveling wave tubes, and gyrotrons [4].

Microwave processing of ceramics was first reported in 1968 by Tinga and Voss [5]. However, it was not until the 1980s that high temperature processing with microwave energy started gaining much ground [6]. Although microwave processing of advanced ceramic materials is still developing, it offers many advantages over conventional ceramic processing

methods such as reduced heating times and lower power consumption [7].

In traditional thermal material processing, energy is transferred by convection and radiant heat onto the surface of the material and then through the material by conduction heating. Materials requiring long processing times via traditional methods undergo thermal gradients within the material, wherein the surface of the material is exposed to more heat than the core of the material, resulting in surface damage [8]. However, in microwave thermal processing, heat is directly transferred to the material volumetrically by molecular interactions with the electromagnetic field. Since the diffusion of heat through the surface, as in traditional thermal processing, is bypassed by volumetric heating, uniform heating and fast processing times can be achieved with heating rates as high as 1000°C/min [8–10].

The major advantages of microwave processing over conventional heating methods are reduced thermal gradients within the material, faster reaction times, lower processing temperatures, high density microstructures, and improved

mechanical properties [11, 12]. These advantages strongly support the use of microwave thermal processing for advanced materials development.

The forcespinning (FS) process is a rapid method to produce nanosize to micron size fibrous materials. Unlike electrospinning, yields as high as 1 g/min in a lab scale unit are easily achieved. The combination of this fiber making technology with the fast heating rates of MW irradiation provides a rapid route for producing ceramic materials. FS utilizes centrifugal forces to overcome shear forces promoting fiber elongation. Process, theory, and schematics have been reported elsewhere [13–15]. In this research, the development and optimization of the parameters involved in the production of  $\beta$ -SiC fine fibers were carefully analyzed and developed materials characterized. The prepared green fine fibers were spun from polymeric precursors.  $\beta$ -SiC nanomaterials have been intensively studied given their unique properties such as high mechanical strength, high thermal conductivity, low thermal expansion coefficient, and chemical inertness when compared to those of their bulk counterparts [16]. In this case, the utilization of a fibrous morphology also provides a significant increase in surface to volume ratio. Many studies have shown the potential applications of  $\beta$ -SiC fine fibers and the lab scale results have shown promising applications; therefore, scientists are researching new and easier methods to develop  $\beta$ -SiC nanostructures.

The preceramic fine fibers were developed utilizing a solution of polystyrene and polycarbomethylsilane. The developed nonwoven fine fiber mats were characterized by FESEM (field emission scanning electron microscope), XRD (X-ray diffraction), EDS (energy dispersive spectroscopy), and FTIR (Fourier transform infrared spectroscopy).

## 2. Experimental

**2.1. Materials.** Polystyrene (PS) with a molecular weight of 280,000 g/mol and polycarbomethylsilane (PCMs) with a molecular weight of 800 g/mol were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used as received. Toluene was purchased from Fisher Scientific (Waltham, MA, USA) and used as received. The PS/PCMs/Toluene (15, 20, and 25 wt% of PS with a 2:1 ratio of PS : PCMs) solutions were prepared inside a MBRAUN (Stratham, NH) glovebox under nitrogen atmosphere in order to prevent oxidation. The solutions were prepared in 20 mL scintillation vials and sealed with parafilm to prevent solvent evaporation. Solutions were magnetically stirred for a period of 4 hours.

**2.2. Fine Fiber Development.** A FS system was placed inside a glovebox under nitrogen environment. Approximately 2 mL of solution was inserted into a cylindrical type spinneret using a 10 mL syringe. The spinneret was outfitted with 30 gage needles. The angular velocity at which the fibers were spun was varied from 5,000 rpm to 9,000 rpm. The solution was depleted in less than 30 sec. The fibers were deposited on a circular collector having 16 equally spaced polytetrafluoroethylene (PTFE) bars. The developed fibers were stored in a glovebox to prevent fiber oxidation.

Fibers were cross-linked to maintain geometric integrity of the precursor fine fibers because PS reaches the glass transition temperature before the preceramic polymer (PCMs) is converted to ceramic SiC during heat treatment. The collected fine fibers were placed under a 254 nm wavelength UV light source for a period of 24 hours. The cross-linking was performed in a glovebox under nitrogen environment.

**2.3. Microwave Pyrolysis.** A microwave furnace, Hi-Tech single mode microwave applicator, was used. The system is fitted with a MH 2.0 W-S water cooled magnetron head assembly. It supplies 2 kW of adjustable microwave energy at 2.45 GHz. The magnetron outputs into a WR340 waveguide. An Omega iSeries iR2 infrared pyrometer was used to record the temperature. The samples were placed between small SiC susceptor plates which absorb electromagnetic energy and convert it to heat. The sample chamber was fitted with a quartz tube attached to a turbo pump. The microwave heating was carried out under nitrogen gas after evacuation of air with the turbo pump. Power was increased 100 W every 4 minutes up to 600 W. The total processing time at 600 W was 3 minutes. The temperature was observed to be approximately 1140°C at 600 W.

**2.4. Fiber Characterization.** Fiber morphology was analyzed using the Carl Zeiss Sigma VP scanning electron microscope. Fiber diameters were measured using the Carl Zeiss Axio-Vision software. For the X-ray diffraction analysis, a Bruker AXS D8 diffractometer was utilized. The fine fibers were scanned from 20 to 80° (2 $\theta$  angles) using a 2D detector. FTIR-ATR with a diamond tip was carried out using an Agilent Technologies Cary 600 Series FTIR spectrometer.

## 3. Results and Discussion

The optimization of the SiC fiber precursors was conducted in a previous study [17]. This study focused on developing highly crystalline  $\beta$ -SiC fine fibers through conventional pyrolysis methods. Several parameters were evaluated that resulted in fibers with average diameters ranging from 270 nm to 2  $\mu$ m. It was concluded that the parameters that synergistically contributed to the development of homogeneous, high yield, bead-free continuous green SiC fibers were of a polymer concentration of 20 wt% in the developed solution which was then processed at an angular velocity of 7000 rpm. Figure 1 shows a nonwoven fine fiber mat with its observable corresponding fiber diameter distribution. Figure 2 shows an SEM micrograph of the precursor fibers showing micron and submicron size fibers. Fiber-fiber adhesion can be observed as indicated by the red boxes. The above mentioned fiber spinning parameters were selected to prepare samples utilized in this work to further analyze the effect of heat treatment via microwave energy processing.

The materials in this study consisted of PS and PCMs with molecular formulas  $(C_8H_8)_n$  and  $(C_2H_6Si)_n$ , respectively. At temperatures between 550°C and 800°C, the precursor becomes an inorganic material as it begins to decompose Si-H, Si-CH<sub>3</sub>, Si-CH<sub>2</sub>-Si, H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub> species which

TABLE 1: Corresponding XRD peak list from Figure 3.

Pos.[°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]	Matched by
26.7407	197.39	3.33386	9.92	04-014-0337
35.6177	1989.65	2.5207	100	00-029-1129
41.4258	111.8	2.17973	5.62	00-029-1129
59.9538	501.03	1.54295	25.18	00-029-1129
71.7441	328.15	1.31564	16.49	00-029-1129

Pos = position of the peak on the  $2\theta$  axis in the XRD spectra.

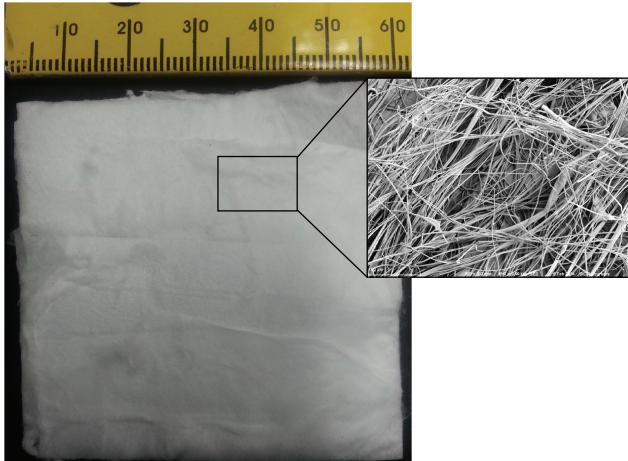


FIGURE 1: 6 cm  $\times$  6 cm SiC precursor mat obtained after 30 sec.

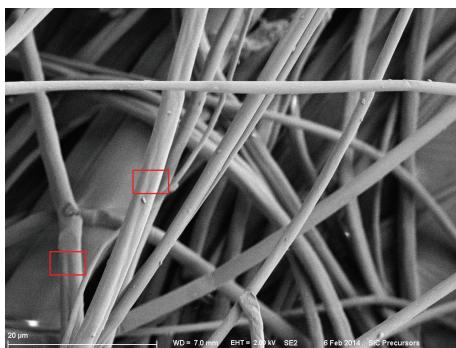


FIGURE 2: SEM micrograph of SiC precursors. Red boxes show fiber surface roughness.

are eliminated from the precursor [18–20]. Increasing the temperature from 800°C up to 1000°C results in amorphous SiC while crystalline SiC begins to form at 1000°C with the evolution of H<sub>2</sub> [18].

XRD results are shown in Figure 3 with a corresponding peak list given in Table 1. The peaks indicate conversion of precursor to  $\beta$ -SiC with  $2\theta = 35.62^\circ$ ,  $41.42^\circ$ ,  $59.95^\circ$ , and  $71.74^\circ$  (reference code: 00-029-1129) ascribed to lattice planes (111), (200), (220), and (311), respectively [21]. Additionally, the slight broadening base of the peaks is indicative of either unreacted material or some amorphous SiC remaining in the sample. A small carbon peak is noted at  $2\theta = 26.74^\circ$  (reference code: 04-014-0337).

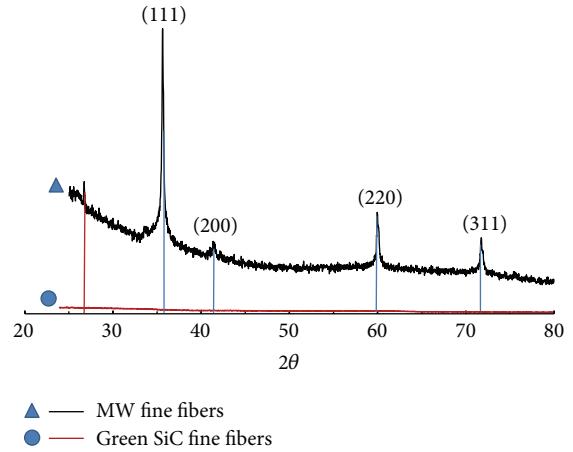


FIGURE 3: XRD spectra of fine fibers before and after microwave assisted heating.

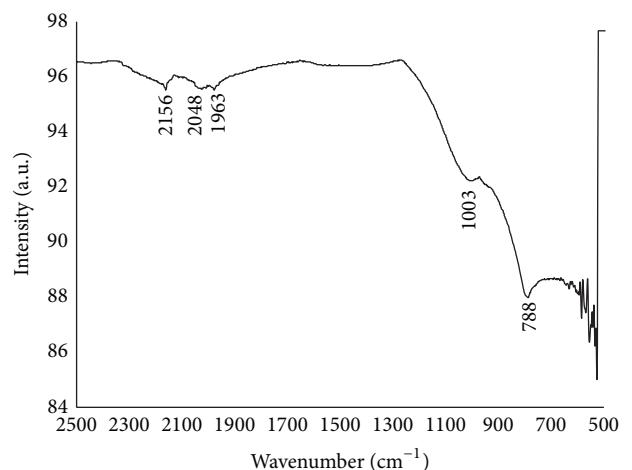


FIGURE 4: FTIR of SiC fine fibers after microwave irradiation.

SiC FTIR reflectance bands can be seen between wave numbers 740 and 970 cm<sup>-1</sup> [22–24]. The FTIR scan shown in Figure 4 depicts a reflectance band at wave number 788 cm<sup>-1</sup>, supporting ceramic conversion of precursor fine fibers shown in Figure 3. The peak at wave number 1003 cm<sup>-1</sup> corresponds to Si-O bonds indicating the presence of SiO<sub>2</sub> in the sample [25, 26]. Although the SiO<sub>2</sub> was not detected in XRD results, it may be due to the nanosized geometries of its content. If the uncured precursor is exposed to oxygen during handling,

TABLE 2: EDS of SiC precursor and microwaved fine fibers.

Element	SiC precursor NFs		Microwaved NFs	
	wt%	at%	wt%	at%
Si	17.63	8.71	37.19	21.32
C	68.99	79.69	46.29	62.06
O	13.38	11.6	16.52	16.62

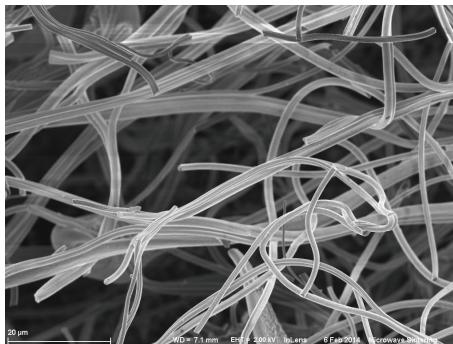


FIGURE 5: SEM micrograph of ceramic converted fine fibers.

oxidation of Si–H and Si–CH<sub>3</sub> can occur resulting in the formation of Si–O–Si bonds [27]. The available oxygen species in the precursor can then form amorphous SiO<sub>2</sub> at temperatures below 1200°C [19]. EDS was performed in the precursor fiber as well as in the ceramic converted fibers. The small presence of oxygen in both samples is given in Table 2. Reflectance band at 2156 cm<sup>-1</sup> is consistent with MeSiH<sub>3</sub> [28] while bands seen at 2048 cm<sup>-1</sup> and 1963 cm<sup>-1</sup> indicate the presence of CO species [29].

These types of composite materials have applications in nanoelectronics, nanomechanics, reinforced composite materials, and nanosensors to mention some [30]. More importantly, these materials may be used to improve SiC/SiO<sub>2</sub> bonding interfaces for improved performance in electronic devices [31, 32]. SiC/SiO<sub>x</sub> materials have been previously synthesized including the use of microwave irradiation [21, 33–36]. However, in these studies Si, SiO<sub>2</sub>, and graphite powders were used as the precursor materials rather than a preceramic polymer. An SEM micrograph of the converted ceramic fine fiber is shown in Figure 5. Micron and submicron size fibers can be seen in this figure. Also, noted is a rough fiber structure in some areas which may be due to adhesion of two or more fibers forming ribbon-like fibers or shrinkage that a fiber undergoes as a result of volatilization of solvent during microwave processing as previously observed in annealed fibers [37]. The micrograph also shows many short fibers, although fibers are expected to be up to 6 feet in length [14]. The precursor fine fibers are removed with tweezers resulting in broken fibers before being placed on the susceptor for MW processing. A continuous deposition method with subsequent MW treatment will preserve fiber length. Figure 6 shows a SEM micrograph of a single SiC nanofiber.

FIGURE 6: High magnification SEM micrograph of a  $\beta$ -SiC fine fiber.

## 4. Conclusion

In this study, we successfully show ceramic conversion of spun PS/PCMs fine fibers to  $\beta$ -SiC fine fibers utilizing forcespinning technology for rapid fiber development and microwave energy processing for rapid ceramic conversion of spun fibers. The combination of these two technologies illustrates a processing route that can be utilized to produce rapid novel ceramic nanomaterials. XRD and FTIR results confirmed ceramic conversion of the fine fibers. Both micron and submicron fibers were observed in SEM images.

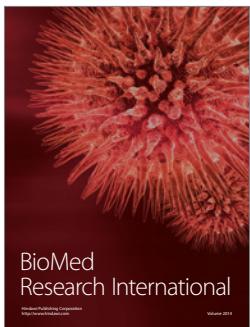
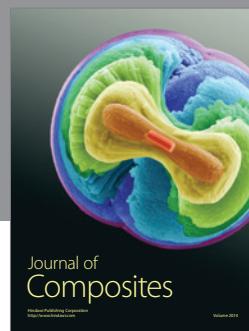
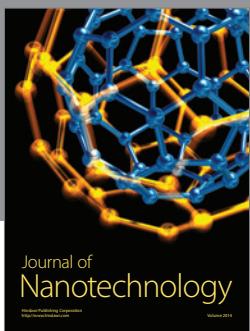
## Conflict of Interests

Dr. K. Lozano and The University of Texas-Pan American have research-related interest in FibreRio Technology Corporation.

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