



# Comparison of microwave and conventional heating methods in carbonization of polyacrylonitrile-based stabilized fibers at different temperature measured by an in-situ process temperature control ring



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## ABSTRACT

The pre-oxidized fibers were carbonized by microwave heating and conventional heating, respectively. The temperature in the two processes was calibrated by a process temperature control ring that was wrapped by the fibers. The microwave carbonized fibers (MCFs) fabricated at 750–1000 °C possess the higher carbon content, larger average crystallite dimensions ( $L_a$  and  $L_c$ ), higher porosity, and more homogeneous structure along cross-section than those of conventionally carbonized fibers (CCFs) obtained at the same temperature. However, when the temperature reaches 1000 °C and above, the crystallite sizes of MCFs are smaller than those of CCFs fabricated at the same temperature, and the difference between the skin and core structure becomes larger as the temperature increases for MCFs. The tensile strength and modulus of MCFs are higher than those of CCFs obtained at 750–1000 °C, while the mechanical properties for MCFs and CCFs obtained at temperature above 1000 °C is close. This phenomenon could be attributed to the temperature dependence of microwave adsorption ability of the as-obtained CFs.

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## 1. Introduction

Carbon fibers (CFs) are utilized increasingly in fields ranging from the aerospace industry to sport products, due to their superior properties including, but not limited to, high specific strength, excellent heat resistance and corrosion resistance. Polyacrylonitrile (PAN) fibers are one of the most important precursors for the production of high-performance CFs. Although CFs have a superior tensile strength, the practical mechanical property, especially the tensile strength of CF is far lower than the theoretically predicted value. The strongest CFs commercially available, the T1000 CFs possess a tensile strength of 7.06 GPa and a Young's modulus of 290 GPa. However, based upon the properties of carbon-carbon bonds, the theoretically predicted values of tensile strength and Young's modulus for CFs are ~180 and ~1000 GPa respectively [1]. It has been well established that the excellent performance of CFs is

closely related to their microstructures resulted from the spinning, oxidative stabilization and carbonization of PAN precursor fibers. In order to further improve the mechanical properties and reduce the manufacturing cost of the CFs, extensive efforts have been focused on the development of manufacturing processes. For example, oxidative stabilization via consecutive irradiation treatments is regarded as an efficient and fast method to reduce the stabilization time and obtain a high yield of high-quality CFs. The effects of irradiations on the microstructures of PAN fibers via electron beam [2,3] and  $\gamma$ -ray [4–6] have been investigated to evaluate the potential application of irradiation technology in producing CFs. Moreover, alternative method for the carbonization process such as microwave heating has also been considered as a more rapid and energy saving method compared with conventional heating [7,8].

Microwave belongs to a portion of the electromagnetic spectrum with wavelengths from 1 mm to 1 m with corresponding frequencies between 300 MHz and 300 GHz. As a new heating method, microwave has been used to process a wide variety of materials including polymers, ceramics, chemicals (organic and

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inorganic) etc. [9–11]. Microwave provides a unique method of transferring energy from source to the material compared with conventional heating. In conventional processing, the heat is generated from the source and then transferred from the external to internal part of material through convection, conduction and radiation, which is comparatively slow and inefficient. In contrast, the microwave heating occurs through the conversion of electromagnetic energy into heat within the irradiated material, which is a process of energy transfer instead of heat transfer and heating from the interior of the material body. The microwave energy is absorbed by materials volumetrically and often selectively with the excellent efficiency of heating and reduced treatment time [12–14]. Moreover, the opposite temperature gradient is established in both heating systems since material is at a much higher temperature than its surrounding during microwave heating, unlike conventional heating where it is necessary for the conventional furnace cavity to reach the operating temperature and begin heating the material [14].

The dielectric materials can dissipate electromagnetic wave to produce heat. The heating mechanism of dielectrics takes place by dipolar and interfacial polarization effects. The polar molecules, such as water, can rotate and try to align in both permanent and induced dipoles with an alternating electric field of microwave. The increased molecular rotation generates friction there by resulting in heat loss. In the case of dielectric carbon-based material having free moving charged particles confined to fixed regions within the material, such as  $\pi$ -electrons, the current travels in phase with the induced electromagnetic field. These  $\pi$ -electrons cannot pair to the phase changes of the electric field; energy is then dissipated in the form of heat called Maxwell–Wagner polarization (interfacial polarization effects) [14–16]. The solid carbon material, which has free moving  $\pi$ -electrons, can be heated by microwave energy. This has become the foundation for the use of ‘unconventional’ microwave heating in production, regeneration and modification of carbon materials [14].

Most of the studies in microwave-assisted carbon preparation utilized microwave input power and irradiation time as the operating conditions. However, they are not representative and adequate to be used as the scaling-up parameters. The bulk temperature monitoring of the carbonaceous precursors has frequently been highlighted as a major problem in microwave-assisted carbon preparation. The use of standard thermocouples inside microwave fields has long been prohibited due to the enhanced localized heating around the thermocouple tip which will give rise to false readings. Meanwhile, the use of infrared is not representative as it only measures the temperature at the surface of microwave heating system. The temperature deviation between the bulk and the reactor surface is due to dielectric properties of the reactant and the reactor, as well as the heating mechanisms [13,16]. Thus, the concrete comparison between the conventional heating and microwave heating could not be realized. The process temperature control ring is a highly accurate ceramic temperature indicator which records the true heat treatment received by the fired product. It takes account of both radiate and transferred heat, as well as the effects of temperature over time. When exposed to heat in the kiln, the ring contracts and continues contracting as the top temperature is maintained over time. The degree of contraction is almost linear over the complete operating range of the ring, providing a practical measure of the accumulated heat to which the ring and the fired products have been subjected. The amount of ring diameter shrinkage can be converted to ‘ring temperature’ for ease of comparison and correlation to the firing process.

H. Lee et al. [7,8] have recently reported that the CF carbonization process using microwave plasma has the potential to not only decrease the consumed energy but also to realize the mechanical

properties of the CF as well as conventional carbonization methods. However, there has been little true development in understanding of the microwave effect on the CF carbonization, other than the empirical consensus that the microwave heating is more rapid and energy saving than the conventional heating method. In this work, the pre-oxidized fibers were carbonized by microwave heating and conventional heating, respectively, the temperature in the two processes was calibrated by the process temperature control ring that was wrapped by the CFs. The microstructure and composition evolution of the obtained fibers were monitored and compared in the two processes under different ring temperatures to get better understanding of the microwave effect on the CF carbonization.

## 2. Experimental section

### 2.1. Stabilization and carbonization

The precursor fibers (PFs) with each single tow containing 1000 filaments, 11.2  $\mu\text{m}$  average diameter, 0.766 GPa tensile strength, 8.7 GPa Young's modulus and 65.7% crystallinity were wet-spun from a copolymer of acrylonitrile/acrylamide/methyl acrylate and supplied by Jilin Carbon Valley Carbon Fiber Co., Ltd. (Jilin, China). The PFs were tied on a ceramic rod to keep fixed length and stabilized for 1 h after heating in air to 270  $^{\circ}\text{C}$  at a heating rate of 1  $^{\circ}\text{C}/\text{min}$ . The stabilized fibers (SFs) were carbonized in high purity Ar atmosphere with a heating rate of 5  $^{\circ}\text{C}/\text{min}$  to different temperatures ranging from 680 to 1285  $^{\circ}\text{C}$  in an industrial microwave furnace (2.45 GHz) to obtain microwave carbonized fibers (MCFs). The schematic diagram of microwave furnace system is shown in Fig. 1. For comparison, the SFs were also subjected to conventional carbonization at the same temperature range with the same heating rate to obtain conventionally carbonized fibers (CCFs). In two carbonization processes, the CFs were all maintained at the final temperature for 1 h. The CFs were randomly placed in the furnace, neither tension nor load was applied to the fibers during above two carbonization processes, and the temperature was calibrated by FERRO process temperature control ring that was wrapped by the CFs. Note that the temperature mentioned in this work for the microwave and conventional heating is the ‘ring temperature’. The CFs obtained in above two processes was denoted as MCF-x or CCF-x, where x represents the ring temperature.

### 2.2. Characterization

Fourier transform infrared (FTIR) spectrum was obtained in a Thermo Scientific Nicolet iN10 spectrophotometer using a KBr pellet with the scanning range from 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ . CFs were grinded into powders and subjected to X-ray diffraction (XRD) measurements on a Rigaku-DMAX2200PC diffractometer by using Cu  $K\alpha$  radiation with  $2\theta$  in a range of 10–80 $^{\circ}$ . The height of the stacking domains ( $L_c$ ) can be determined using the (002) FWHM  $2\theta$  values and the Scherrer equation:  $L_c = K\lambda/(\beta_{002} \times \cos\theta_{002})$ , where  $\beta_{002}$  is the line breadth (FWHM) in radians with the instrumental broadening subtracted,  $\lambda$  is the X-ray wavelength which is equal to 1.5418  $\text{\AA}$ , and the coefficient K taken to be 0.89 and  $\theta_{002}$  is the diffraction angle of the peak of (002) reflection. The interlayer spacing ( $d_{002}$ ) was calculated from the Bragg peaks using the Bragg law:  $\lambda = 2d\sin\theta_{002}$ . Raman spectra were examined on a Thermo Scientific DXR Raman microscope spectrometer with a laser wavelength of 633 nm, a laser power of 3 mW and an exposure time of 10 s over three accumulations. A bundle of fibers was embedded in epoxy resin. The incident laser beam was focused on the transverse section of the fiber under the microscope, and then the laser spot with a diameter of about 2  $\mu\text{m}$  was scanned along the radial direction with a scanning step length of 1  $\mu\text{m}$ . Schematic diagram of

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