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Microwave plasma carbonization for the fabrication of polyacrylonitrile-based carbon fiber

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ABSTRACT

Microwave heating is investigated as an alternative method of carbonization process for carbon fiber (CF) in order to reduce the energy costs. In this study, a microwave plasma system is designed for the carbonization process, and stabilized polyacrylonitrile fiber is carbonized using the system. Compared with the CF fabricated by conventional thermal carbonization process, plasma-carbonized CF has higher surface roughness, which can enhance the mechanical interlocking between resin and CF and increase the mechanical properties of the CF Reinforced Polymer (CFRP). Furthermore the mechanical properties of the CF didn't fall behind that of the conventionally carbonized one. As a result, microwave plasma carbonization is a good candidate for the next-generation carbonization processes in the CF industry.

1. Introduction

Carbon fiber (CF) is an attractive material in aerospace engineering, vehicle manufacturing, and construction, due to its lightweight characterization and good physical properties such as good mechanical, thermal, and electrical properties [1,2]. BCC Research reported that the CF market is expected to grow 6.3% annually until 2016, but possibly would grow even more rapidly if the price of carbon fiber, which is currently USD30-40 per kilogram, was reduced [1,3].

Most CF is manufactured using polyacrylonitrile (PAN) precursor because the PAN-based CF is stronger [4] than other low cost precursors such as textile-grade PAN [5] and lignin [6,7]. The PAN-based precursor undergoes an oxidative stabilization process in an oxidative atmosphere and then a carbonization process in an inert atmosphere in order to be converted into CF [2]. Because a high level of thermal energy is required in the CF processes, particularly for the stabilization and carbonization, which amounts to 45% of the total production cost, alternative processes are being investigated in order to reduce the CF process cost. Atmospheric pressure plasma [8,9] and electron beams [10] have been investigated as alternative methods for the stabilization process and microwave plasma [11,12] has also been considered for the carbonization process.

Microwaves are electromagnetic waves with a frequency ranging from 300 MHz to 300 GHz. When microwaves are radiated into a material, the material temperature can be directly increased by dipolar polarization or interfacial polarization [13], or indirectly increased by heat transfer from the plasma discharge around the material. Due to the reduced path of the heat transfer, microwave heating can be a more rapid and energy saving method of heating compared with conventional heating [13,14].

On the other hand, microwave can be used as energy sources not only for heating materials but also for discharging plasma for various material process. In 1983, M. Kamo et al. used microwave plasma system to grow diamond structure on non-diamond substrate [15]. C. Bower et al. reported the growth of carbon nanotube using microwave plasma-enhanced CVD in 2000 [16]. Microwave plasma system could be used for doping of films such as cuprous oxide films nitrogen doping by Z. Zang et al. [17]. The application of microwave plasma system in the etching of silicon was reported in 1987 by S. Tachi et al. and now is being adopted in semiconductor industry [18].

In the carbon fiber process, Oak Ridge National Laboratory first proposed the concept of a microwave-assisted plasma carbonization process for CF manufacture through two patents [12].

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However, there are few papers published on the feasibility and the characteristics of the CF manufactured using the microwave plasma carbonization. In this study, a microwave plasma system is designed and fabricated for the microwave plasma carbonization process. The characteristics of the CF manufactured using microwave plasma carbonization are analyzed in order to investigate the feasibility of microwave plasma carbonization.

2. Experimental section

2.1. Fabrication of the microwave plasma system

The microwave system for the carbonization process comprises a magnetron, a waveguide, two chambers, and a dual quartz cylinder system. A schematic of the system is presented in Fig. 1. The magnetron head (GA4002A, Gerling Applied Engineering, Modesto, CA, USA) generates a 2.45 GHz frequency microwave, which is emitted through a waveguide with three stub tuners (WR284; Gerling Applied Engineering, Modesto, CA, USA) that are adjusted to minimize the reflection of the microwave power back to the magnetron. During plasma carbonization process, the tuners are real time controlled to make more than 95% of the input power is transferred to discharge plasma. The dual quartz cylinder system was composed of an inner quartz cylinder with a 23 mm inner diameter and an outer quartz cylinder with a 35 mm outer diameter surrounding the inner quartz cylinder. The length of the both cylinders was 1000 mm. Compressed air was flown between the two quartz cylinders in order to protect quartz and vacuum components such as the O-ring from melting, which is the purpose of adopting a dual quartz cylinder system. The waveguide is penetrated by the dual quartz cylinder system and the electromagnetic wave energy is transferred via the waveguide from the magnetron to the quartz cylinder system. In order to carbonize a strand of stabilized PAN fiber inside the inner quartz tube, the fiber was fixed in the center axis of the dual quartz cylinder system and plasma discharge is induced in the tube by the electromagnetic energy. A gas injector unit is inserted into the dual quartz cylinder system 25 cm from one end in order to inject argon gas (99.999%) inside the cylinder. The two chambers connected to each end of the dual quartz cylinder system have roller systems, to mount stabilized PAN fiber on them. The chambers are vacuumed with a rotary pump to get rid of oxygen in it and make inert atmosphere for carbonization process.

2.2. Characterization of the fabricated microwave plasma

A handmade dual Langmuir probe (DLP) was installed inside the dual quartz cylinder system in order to measure the bulk plasma parameters during the carbonization process [19]. The probe had two tungsten tips with a 1 mm diameter and 7 mm length. The voltage between the tips was scanned using an electronic system (DLP2000, Plasmart, Korea) in order to measure the plasma parameters from mathematical fitting of the obtained I–V curve.

In the carbonization process, the process temperature can have a significant influence on the CF properties because the mechanical properties of the CF, such as the tensile strength and Young's modulus, increase significantly as the carbonization temperature increases [20]. The change of the gas temperature during the microwave plasma discharge was measured using a K-type thermocouple placed in the center of the quartz cylinder.

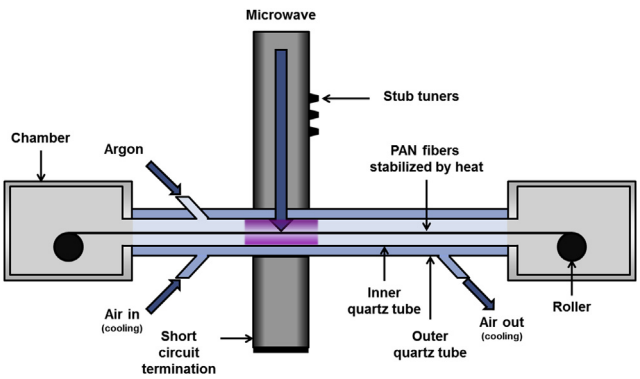

Fig. 1. A schematic of the microwave plasma system for the carbonization process.

2.3. CF preparation

The precursor used in the experiment is a commercial itaconic acid-modified PAN fiber consisting of 3000 filaments and it was supplied by Sinosteel Jilin Carbon Co., Ltd. (Jilin, China). Before the microwave plasma carbonization and thermal carbonization, the precursor was thermally stabilized for 140 min in a lab-made system for a continuous CF stabilization process [21,22]. In the stabilization process, the precursor passed through ten heating zones with the temperature increasing from 200 to 295 °C. A Fourier transform infrared (FT-IR) spectroscopy (Nicolet iS 10, Thermo Fischer Scientific, USA) was used to verify the stabilization reaction. The wave number of the IR absorption spectra was scanned in the range of 400–4000 cm^{-1} at a resolution of 1 cm^{-1}.

After the stabilization, two types of carbonization processes, i.e. the conventional thermal carbonization and microwave plasma carbonization, were performed. The conventional carbonization process was conducted in a tubular furnace (Korea Furnace Development Co. Ltd, Korea) filled with 99.999% N_2 to atmospheric pressure. The furnace temperature was increased at a heating rate of 5 °C/min until the maximum temperature of 800 °C. The fiber inside the furnace was unloaded after the furnace cooled naturally to room temperature. In contrast, the microwave plasma carbonization was conducted in a microwave plasma system filled with 99.999% Argon flowed at 3 lpm to a pressure of 5 Torr. The transmitted microwave power for the discharge was 100, 200, 500, and 1000 W, and the stabilized PAN fiber loaded inside the quartz cylinder was carbonized using the microwave plasma for 5 min. Then, the fiber inside the plasma system was unloaded after the plasma system cooled naturally to room temperature.

2.4. Characterization of the prepared CF

In order to verify the effect of the microwave plasma-assisted carbonization process on the stabilized PAN fiber, the carbon fiber filaments were sampled at the length of 50 mm in the intersection position of waveguide and quartz tube after plasma carbonization process. Raman spectroscopy (LabRAM HR 800, Horiba Jobin Yvon, Japan) was conducted with the 514 nm Ar ion laser with 100 × objective lens. The tensile strength and modulus of the CF were measured using a universal testing machine (UTM; Instron Universal Tester 5567, Instron, USA). Thirty filaments from each CF sample were tested at a rate of 2 mm/min using ±2.5 N of load cell, and the gauge length was 25 mm.

The diameter of the CF filaments was observed using an optical microscope (BX51, Olympus, Japan) in order to calculate the mechanical properties. The surface of the prepared CF was observed using a scanning electron microscopy (SEM; Nova NanoSEM 450, FEI, Czech Republic; S-4700, Hitachi, Japan) with magnifications of 3000 and 3500.

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