Carbonization performance of pre-oxidized PAN fibers prepared by microwave heating

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Abstract. We have carbonized the modified PAN fibers which coated with a hybrid microwave absorbent and pre-oxidized by microwave heating for 50 min. The carbonization process of pre-oxidized CB/S-PAN fibers process was performed under nitrogen atmosphere at different temperatures. The carbonized fibers were characterized by mean of Raman spectroscopy, elemental analyzer, X-ray diffraction (XRD), thermogravimetric analyzer (TGA), mechanical tester, and scanning electron microscopy (SEM). The results indicated that more ordered crystal structure and highly graphitic content was obtained at 950°C, arise from the formation of aromatic structures. The fibers’ surface appeared roughly without defects suggesting a strong graphitic structure. This rough nature which results from the deposition of nanoparticles at an earlier stage before the pre-oxidation and the microwave penetration can strongly improve the interlocking between the fibers and matrix in the carbon fibers’ composites.

1. Introduction
Carbon fibers (CF) have attracted considerable attention due to their high mechanical properties, light weight, good chemical and thermal resistance, and excellent electrical and thermal conductivity [1-6]. Carbon fibers can be classified based on the precursor types into polyacrylonitrile (PAN)-based CFs, pitch-based CFs, and rayon-based CFs. The commonly used precursor is PAN due to its higher melting point [7], relatively lower cost, and greater carbon yield [8]. The conversion process of PAN precursor into CFs involved two main stages: pre-oxidation where the linear structure is transformed into conjugated ladder structure [9] and carbonization where a graphite layer structure is formed [10].

Many researches concentrated on studying the thermal pre-oxidation and subsequent carbonization [11] of CFs. A few studies about the optimization of PAN conversion process have been done [12]. Kim et al [13] introduced a new microwave plasma system for the carbonization process which resulted in higher surface roughness. In our previous study, hybrid nanoparticles (Carbon black/SiC) were used as microwave absorbent and coated onto the surface of the PAN fibers in order to improve their microwave absorbability. Typical new microwave system was designed and used to induce the pre-oxidation process for the modified CB/S-PAN fibers. The results showed that the cyclization reaction was accelerated and cyclization degree was optimized [14]. In this work, structural evolvements in the conversion of microwave pre-oxidized CB/S-PAN fibers into CFs as well as the influences of fibers modification on the carbonization
performance were investigated.

2. Experimental

2.1. Material
The CB/S-PAN fibers used in this study were modified in our laboratory. The modified PAN fibers were pre-oxidized at low temperature (110-170°C) by microwave heating. In the process of carbonization, the pre-oxidized fibers were passed through a tubular furnace with a ceramic tube (length: 1 m). The pre-oxidized fibers were carbonized at different temperature (550°C, 750°C, and 950°C) in nitrogen (N₂) with a flow rate of 3-5 L/min.

2.2. Characterization
The surface structure was analyzed by Raman spectra (inVia-Reflex, Japan). The elements’ content was measured by Vario EL III elemental analyzer (Germany). The phase structures were detected by X-ray diffraction (XRD, D/max 2550 PC, Japan). Gravimetric thermal analysis (TGA) was carried out using Discovery TGA (Q5000IR) instrument. A XQ-1 computerized mechanical tester was used for mechanical analysis. The morphology was studied by field emission scanning electron microscopy (FESEM, JSM-5600LV, Japan). Results and discussion

3. Results and discussions

3.1. The evolution of chemical structure
Raman patterns of carbonized CB/S-PAN fibers were presented in figure 1. Two characteristic peaks were found, Raman-allowed band around 1580 cm⁻¹ assigned to the graphitic structure (G-mode) and disorder-induced band around 1360 cm⁻¹ (D-mode) which represented disorder carbon structure corresponded to the increase in the amount of unorganized carbon and the decrease in crystal size [15].

![Figure 1. Raman spectra of carbonized CB/S-PAN fibers.](image)

The graphitization degree R which is sensitive to the average distance between defects [16] was characterized by the ratio of the integrated intensity of disorder-induced band to Raman-allowed band (R=ID/IG). The Raman shifts of the G and D peaks and the R values of all samples estimated from Raman patterns are listed in table 1. The R ratio decreased with the increase of
carbonization temperature suggesting the generation of the more ordered crystal structure at 950°C [17,18]. Moreover, it can be noticed that the G band shift to lower wavelength this was due to changes in the relative intensity of D band overlapping [16].

### Table 1. Raman data of carbonized CB/S-PAN fibers.

| Carbonization Temperature (ºC) | D-mode (cm⁻¹) | G-band (cm⁻¹) | R     |
|-------------------------------|----------------|----------------|-------|
| 550                           | 1354.00        | 1580.80        | 2.60  |
| 750                           | 1340.40        | 1580.20        | 1.37  |
| 950                           | 1340.40        | 1574.80        | 1.12  |

At the initial stages of carbonization, crosslinking reactions occurred in the pre-oxidized PAN. The cyclized structure began to link up in the lateral direction by denitrogenation and dehydration. A planar structure can be formed with the basal planes aligned along the fiber axis. HCN and NH₃ released at temperature up to 450°C were from an un-laddered structure while in the range of 450–900°C were from laddered structure leading to polymer crosslinking. The release of N₂ was recognized from 700°C [19]. Goodhew et al proposed that intermolecular dehydrogenation happened in the range of between 400°C and 600°C, while denitrogenation occurred at higher temperatures. Dehydrogenation attached ladder molecules forming graphite-like ribbons, while, denitrogenation was accountable for the growth of ribbons to form sheet-like structures. The sheets could further grow at higher temperatures with the release of N₂ [20]. The chemical composition of the carbonized CB/S-PAN fibers were presented in table 2. As can be seen, a significant effect in the elements was observed. As the carbonization temperature increased the carbon content increased, while nitrogen and hydrogen content decreased by dehydrogenation and denitrogenation. This further revealed the generation of the carbon structure of the carbonized CB/S-PAN fibers.

### Table 2. Elemental composition of carbonized CB/S-PAN fibers.

| Carbonization Temperature (ºC) | Elemental content (%) |       |       |
|--------------------------------|-----------------------|-------|-------|
| 550                            | 68.60                 | 2.40  | 18.24 |
| 750                            | 71.99                 | 1.48  | 16.50 |
| 950                            | 87.33                 | 0.29  | 9.73  |

3.2. Phase analysis

XRD patterns of carbonized CB/S-PAN fibers were presented in figure 2. XRD profile exhibited broad diffraction peaks at 2θ ≈ 25º assigned to (002) crystalline plane, demonstrating the formation of carbon basal plane, and rearrangement of layer plane which changed the microstructure parameters such as crystal height Lc [21]. It can be pointed out that Lc increased and the FWHM values decreased as the carbonization temperature increased (table 3). This finding is correlating with Raman results suggesting the formation of a more perfect graphite structure.

### Table 3. XRD data of carbonized CB/S-PAN fibers.

| Carbonization Temperature (ºC) | 2θ=25º Peak FWHM | Crystallite height Lc (nm) |
|--------------------------------|------------------|--------------------------|
| 550                            | 13.31            | 0.59                     |
| 750                            | 11.93            | 0.66                     |
| 950                            | 5.90             | 1.33                     |
3.3. Thermal stability

TGA curves of carbonized CB/S-PAN fibers at different carbonization temperatures were displayed in figure 3. As shown, a primary weight loss below 200ºC for carbonized fibers at 550ºC and 750ºC was noticed due to the removal of unstable chemical species from the fibers’ surface [22]. A secondary weight loss between 400ºC and 700ºC was observed for carbonized fibers at 550ºC, which can be ascribed to the further release of volatile products due to low carbonization temperature [23]. No obvious weight loss was noticed for carbonized fibers at 950ºC indicating an improved graphite structure.

3.4. Physical and mechanical properties

The mechanical and physical properties of carbonized CB/S-PAN fibers were listed in table 4. The tensile strength and modulus of carbonized fibers increased as the carbonization temperature
increased. Tensile strength is not graphitic order and orientation dependent but is affected by defects [24] and the elementary formation of carbon basal planes [25] which could further grow at higher temperatures with the release of N₂ [20]. The modulus is dependent on the graphitic order which was affected by the increase of the crystal size, therefore in good agreement with Raman and XRD results. The carbonized fibers diameter decreased while the density increased at higher temperature interpreting that the crosslinking of ladder structure, as well as the lengthening and broadening of carbon basal planes, led to the repacking of the structure [26].

| Carbonization Temperature (°C) | Diameter (μm) | Density (cg/cm³) | Tensile strength (GPa) | Tensile modulus (GPa) |
|--------------------------------|---------------|------------------|------------------------|-----------------------|
| 550                            | 7.40          | 1.47             | 0.64                   | 26.93                 |
| 750                            | 7.53          | 1.80             | 0.98                   | 53.96                 |
| 950                            | 6.96          | 1.80             | 1.00                   | 71.06                 |

3.5. SEM observation

Figure 4(a) displayed the surface topography of carbonized CB/S-PAN fibers. As shown, the presence of nanoparticles on the fibers’ surface with aid of microwave penetration during the pre-oxidation process can enhance the surface roughness and consequently the bond strength of fibers/matrix interface during the fabrication of CFs composites. The surface of carbonized S-PAN fibers was uniformly deposited with NPs, indicating the good coupling between NPs and the PAN fibers’ surface. Furthermore, the fibers’ surface seemed free of defects indicating the formation of a strong graphitic structure [27]. SEM images of fracture surfaces for the carbonized CB/S-PAN fibers were presented in figure 4(b). It could be seen that almost similar cross-section regularity was observed. The fracture was seemed to begin in the specific skin area and then transferred to the core. The carbonized fibers possessed brittle fracture surface and this nature became distinct as the carbonization temperature increased. Furthermore, it exhibited somehow smooth surface and random structure at 550°C, and the roughness increased at higher carbonization temperature.

Figure 4. Different magnification SEM fracture morphology images of CB/S-PAN fibers carbonized at (a1) 550°C, (a2) 750°C, and (a3) 950°C. Different magnification SEM topography images of CB/S-PAN fibers carbonized at (b1) 550°C, (b2) 750°C, and (b3) 950°C.
4. Conclusion
The carbonization performance of microwave pre-oxidized CB/S-PAN fibers was studied. The Raman analysis revealed the formation of a graphite structure, while XRD results indicated that the ladder polymer cross-linked to enhance the growth of the carbon basal planes. The elemental analysis further revealed the generation of the carbon structure. The analysis of thermal stability confirmed the formation of a more perfect graphitic structure. The increase of Young’s modulus correlated to the increase of graphitic order and crystal size. The growth of carbon basal planes and the elimination of structural defects lead to the increase of tensile strength.

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