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Effect of additional heat-treatment temperature on chemical, microstructural, mechanical, and electrical properties of commercial PAN-based carbon fibers

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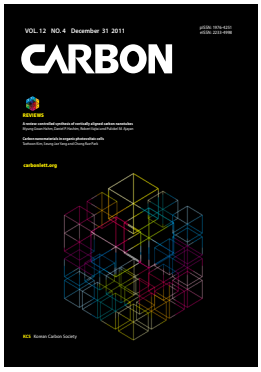

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Abstract

In this present work, the effect of additional heat-treatment (AHT) in the range from 1800°C to 2400°C on the chemical composition, morphology, microstructure, tensile properties, electrical resistivity, and thermal stability of commercial polyacrylonitrile (PAN)-based carbon fibers was explored by means of elemental analysis, electron microscopy, X-ray diffraction analysis, single fiber tensile testing, two-probe electrical resistivity testing, and thermogravimetric analysis (TGA). The characterization results were in agreement with each other. The results clearly demonstrated that AHTs up to 2400°C played a significant role in further contributing not only to the enhancement of carbon content, fiber morphology, and tensile modulus, but also to the reduction of fiber diameter, inter-graphene layer distance, and electrical resistivity of "as-received" carbon fibers without AHT. The present study suggests that key properties of commercial PAN-based carbon fibers of an intermediate grade can be further improved by proprietarily adding heat-treatment without applying tension in a batch process.

Key words: PAN-based carbon fiber, additional heat-treatment, chemical composition, mechanical property, electrical resistivity, microstructure

1. Introduction

It is well known that carbon fibers have excellent multi-properties of thermal, mechanical, thermo-mechanical, thermo-physical, electrical, chemical and frictional properties, particularly in elevated temperatures [1,2]. Therefore, rayon-based, acrylonitrile-based, and pitch-based carbon fibers have been extensively used in a variety of industrial and military applications such as aircraft, aerospace, automobiles, construction, electronics, and the sports and leisure industries due to their distinguishable advantages over glass or organic fibers [2-4]. Among commercial carbon fibers, PAN-based carbon fibers have been of great interest to academia and industries over the world, and have been most widely studied for reinforcing composites [6-10].

As with other carbon fibers, diverse grades [11] of PAN-based carbon fibers are commercially available and vary from manufacturer to manufacturer, depending on the precursor fibers, heat-treatment process, other processing and treatment conditions, end-use, etc. PAN-based carbon fibers are, in general, manufactured in the presence of tension and continuous process inert atmosphere at an industrial level. General-purpose carbon fibers, referred to as high-strength and intermediate modulus grades depending on the heat-treatment temperature, are proprietarily produced under high temperatures between 1300°C and 1600°C in an inert atmosphere [12].

The properties and characteristics of carbon fibers strongly depend on the heat-treatment processes (stabilization, carbonization and graphitization), tension, surface treatment, sizing, etc. [12-16]. Of these variables, final heat-treatment temperature is known to be critically important for producing carbon fibers with better properties. That is, the heat-treatment temperature may significantly alter the chemical, morphological, microstructural, mechanical, thermal and electrical properties of the resulting PAN-based carbon fibers. It is understood that the crystalline structure of carbon fibers becomes ordered and the aromatic molecules therein are aligned more uniformly and densely. As a result, the strength, modulus, and electrical and thermal conductivities of carbon fibers increase as the heat-treatment temperature increases [17-19]. In addition, the fiber morphology is developed with a preferred orientation [20]. Yoon et al. [21] reported earlier that commercial pitch-based carbon fibers were post-heat-treated at high temperatures, significantly increasing some fundamental characteristics through post-heat-treatment.

Therefore, considering of the role of heat-treatment temperature in the preparation of carbon fibers, it may be hypothesized that additional heat-treatment (AHT) at higher temperatures than the processing temperature of commercial PAN-based carbon fibers can not only further enhance their properties, but can also broaden the applicability of commercial or post-consumed carbon fibers. Consequently, the objective of this study is to investigate the effect of AHT carried out in the temperature range from 1800°C to 2400°C on the chemical composition, fiber diameter, fiber morphology, X-ray diffraction (XRD), single fiber tensile properties, electrical resistivity, and thermal stability of commercial PAN-based carbon fibers, and also to diagnose the feasibility of marginal property improvement by AHT without applying tension in a batch process.

2. Experimental

2.1. Materials

Commercial PAN-based carbon fibers (TZ-507, 3K, Taekwang Industries, Korea) were used 'as-received' for high temperature treatment throughout this work. The fibers were used for characterization after high temperature treatment but without sizing treatment.

2.2. AHT of carbon fibers

AHTs of commercial PAN-based carbon fibers was completed through purging high purity nitrogen gas (99.999%) at 1800°C, 2000°C, 2200°C, and 2400°C in a batches using a box-type graphitization furnace of 600 mm × 600 mm × 600 mm in size (ACE Vacuum Inc., Korea). A number of carbon fiber tows were uniformly wound around a graphite rod 150 mm long prior to each heat-treatment. Fig. 1 represents the schematic of the box-type graphitization furnace used in this work.

The carbon fiber tows wound around a graphite rod were placed in the middle of the furnace and the vacuum was applied constantly and continuously during the AHT process. Here, the AHT indicated that commercial carbon fibers, which were proprietarily heat-treated during manufacturing but upon which a final heat-treatment temperature was not performed, were additionally heat-treated at high temperatures above 1800°C in this study. Tension was not applied throughout the heat-treatment. Table 1 summarizes the AHT processing conditions used. The temperature was monitored up to 1200°C by using an R-type thermocouple and a temperature sensor. Preliminary tests showed the instrument had an error margin between the set temperature and real temperature of ±5°C. The heating rate was 500°C/h. Each sample was exposed isothermally to each heat-treatment temperature for 30 min and then naturally cooled to the ambient temperature. The 'as-received' commercial carbon fiber without ADT (untreated) was also used for comparison.

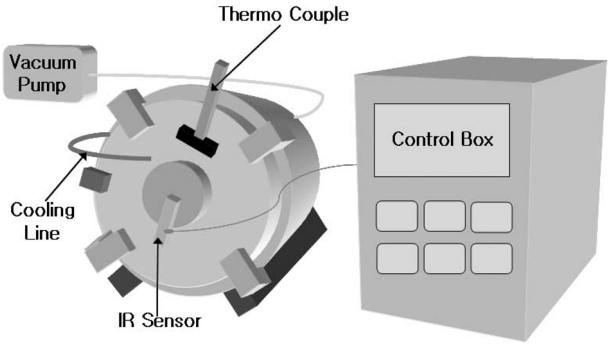

Fig. 1. Schematic illustration of a box-type graphitization furnace used in this work.

Table 1. A summary of AHT processing parameters performed with commercial PAN-based carbon fibers used in this work

Processing parameter	Heat-treatment condition
Final temperature	1800°C, 2000°C, 2200°C, 2400°C
Heating rate	500°C/h
Heating step	One-step up to final temperature
Holding time	30 min at final temperature
Atmosphere	N_2 (99.999%)
Cooling	Natural cooling

AHT: additional heat-treatment, PAN: polyacrylonitrile.

2.3. Characterization

Elemental analysis was performed using an elemental analyzer (Elemental Analyzer, Elementar Vario EL, Elementar Analysensystem, Germany) in order to examine the chemical compositions (C, H, N and S) of untreated and AHT carbon fibers. "Untreated" carbon fibers indicate 'as-received' commercial carbon fibers without AHT, but with the proprietary surface treatment and sizing treatment performed at the place of manufacture, whereas the AHT carbon fibers indicate commercial carbon fibers with AHT processes performed in the laboratory.

The thermal stability of the untreated and AHT carbon fibers was investigated in temperatures up to 1000°C in an inert atmosphere purged with argon gas by means of TGA (Thermogravimetric Analyzer, LABSIS TM, Setaram, France). The heating rate of 20°C/min was used throughout the measurement.

A scanning electron microscope (SEM, S-570, Hitachi, Ja-

pan) was used to observe the fiber diameter and the morphology of the untreated and AHT carbon fibers. Each carbon fiber filament was observed both in the longitudinal and transverse directions. Each sample was coated with Pt in order to avoid a charge build-up and to obtain better images prior to observations.

A high-resolution X-ray diffractometer (X'Pert PRO-MNR, Philips, Netherlands) with a continuous-type scan mode was used to explore the variations in the X-ray diffractogram of each sample. The scanning range of 2θ was 5°~50° and the step size of 2θ was 0.04°. The K_α radiation was used and the targeting material was Cu.

The tensile tests for the untreated and AHT carbon fiber filaments were carried out according to a standard single-filament tensile test method (ASTM D3379-75) by using a universal testing machine (Instron 4467, Instron, USA). A load cell of 2.5 N was used. The crosshead speed was 1 mm/min and the gauge length was 25 mm. The average value of the tensile strength, tensile modulus and elongation at break of each sample was obtained from 20 test results. The average fiber diameter obtained from 10 filament samples each by using SEM was used for calculating the tensile data.

The electrical resistivity of carbon fiber filaments was measured with a two-point probe method according to ASTM B193-87 using an electrical resistivity tester (ASL 800 MEGOHMETER, USA). Each single fiber filament was taken out of the carbon fiber tow. Each filament was placed on top of a glass plate and each end of the filament was fixed with a single drop of silver paste. The average value of the electrical resistivity was obtained from 20 samples of each specimen. The average fiber diameter was obtained from 10 filament samples by using SEM was used for calculating the resistivity.

3. Results and Discussion

3.1. Chemical composition

Table 2 shows the chemical compositions measured for the untreated carbon fibers and AHT carbon fibers heat-treated at 1800°C, 2000°C, 2200°C, and 2400°C. Under comparison, the carbon content increased slightly as the AHT temperature increased from 1800°C to 2400°C, whereas the nitrogen and hydrogen contents decreased under the same conditions. The carbon content increased by about 5% from 92.7% (untreated) to 97.4% (heat-treated at 2400°C), whereas the nitrogen and hydrogen content decreased from 3.53% (untreated) to 0.4% (heat-treated at 2400°C), and from 3.02% (untreated) to 1.28% (heat-treated at 2400°C), respectively.

Table 2. Chemical Compositions measured for carbon fibers untreated and additionally heat-treated at different temperatures

Heat-treatment temperature (°C)	C	H	N	S
Untreated	92.73	3.02	3.53	0.23
1800	97.06	1.08	0.33	0.54
2000	97.35	1.26	0.36	0.65
2200	97.38	1.28	0.39	0.45
2400	97.43	1.28	0.40	0.46

The carbon content of the untreated carbon fiber examined in this work was similar to that of commercial PAN-based carbon fibers of high strength and intermediate modulus grade. Considering of the chemical composition results studied here, we expect that AHTs above 1800°C in this work can change the microstructural, mechanical, and electrical properties of commercial PAN-based carbon fibers of the TZ-507 grade.

3.2. Fiber morphology

Fig. 2 displays SEM micrographs observed in the longitudinal and transverse directions of the carbon fibers untreated and with additional heat treatments at different temperatures. It has been well-established that the mechanical properties of carbon filaments strongly depend on the microstructure of the carbon fiber formed during the carbonization and graphitization

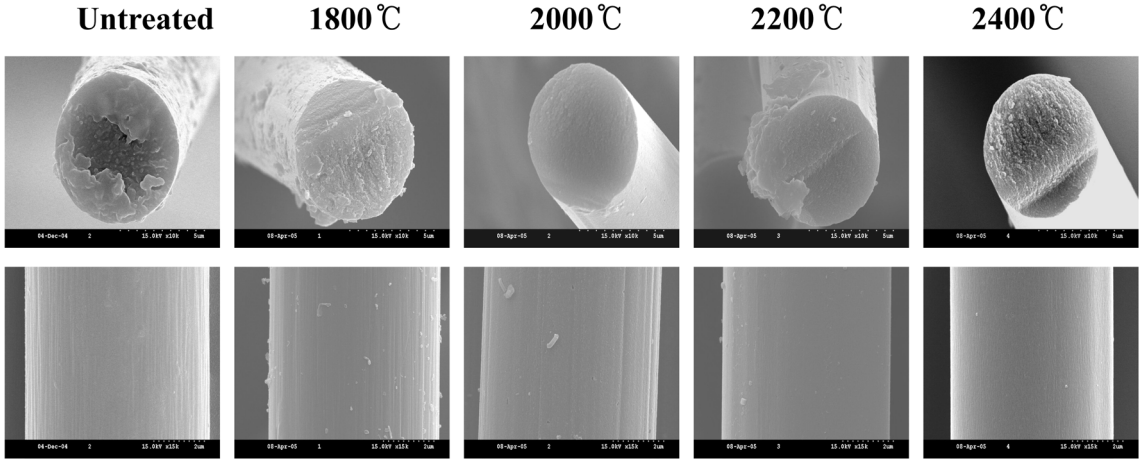

Fig. 2. Scanning electron microscopy micrographs of untreated and additionally heat-treated polyacrylonitrile-based carbon fibers at 1800°C, 2000°C, 2200°C, and 2400°C. Top: transverse direction (×10 000), Bottom: longitudinal direction (×15 000).

Table 3. The average fiber diameters of carbon fibers untreated and additionally heat-treated at different temperatures

Heat-treatment temperature (°C)	Average fiber diameter (μm)
Untreated	6.82
1800	6.64
2000	6.60
2200	6.47
2400	6.26

Table 4. XRD result obtained for carbon fibers untreated and additionally heat-treated at different temperatures

Heat-treatment temperature (°C)	*d*-spacing (Å)	2θ	P/B ratio[a]
Untreated	3.521	25.27	0.844
1800	3.471	25.57	1.728
2000	3.466	25.64	2.012
2200	3.447	25.68	2.642
2400	3.434	25.92	3.535

XRD: X-ray diffraction.
[a]Peak height (counts/s) / background (counts/s).

processes. The extent of the preferred orientation of graphene layers formed along with the fiber axis may influence the tensile modulus of carbon fiber predominantly, whereas the microstructural defects existing on the fiber surfaces in the fiber direction may affect the tensile strength predominantly. It can be seen from Fig. 2 that with increasing AHT temperature the fiber surfaces became uniform and clean, and the fiber striations disappeared. It appeared that the fiber morphology was typical of PAN-based carbon fibers. The sub-micrometer sized particles seen at 1800°C and 2000°C are likely due to artificial impurities or artifacts from the foreign materials existing in the graphitization furnace inside upon the heat-treatment process. At 2200°C and 2400°C, such artifacts were removed and they were rarely found in the images.

Table 3 shows variations in the fiber diameter with additional heat- treatments. The fiber diameter (6.82 μm) of the untreated carbon fiber without AHT was reduced by about 8.2% to 6.26 μm when the AHT temperature was 2400°C. This can be explained by the fact that at 2400°C the inner crystalline layers of the untreated carbon fiber became more aligned and closer together, leading to a decrease of the interspacing distance between the graphene layers and also a decrease of the fiber diameter as well.

3.3. Microstructure

Table 4 shows the effect of AHT on the XRD pattern of the untreated carbon fiber. In general, PAN-based carbon fibers are non-graphitizable, resulting in a turbostratic structure even after heat-treatment at temperatures higher than 2400°C. The 2θ value, which indicates the average distance *d*-spacing between

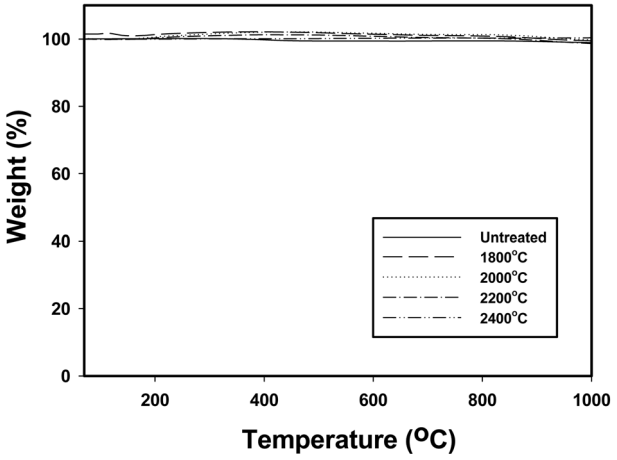

Fig. 3. Thermogravimetric analysis thermograms measured in N_2 for polyacrylonitrile-based carbon fibers untreated and additionally heat-treated at different temperatures.

graphene layers, was decreased from 3.521 Å for the untreated carbon fiber to 3.434 Å for the carbon fiber heat-treated at 2400°C. As the temperature of the AHT increased, the *d*-spacing gradually decreased but did not reach the theoretical *d*-spacing value (3.354 Å) of a perfect graphitic structure. The 2θ gradually increased with the heat-treatment temperature, reaching 26° at 2400°C, approaching a graphite-like structure. It was inferred that no application of tension during the AHT process was responsible for the *d*-spacing greater than 3.4 Å. It may be hypothesized that additional heat- treatment temperatures higher than 2400°C may result in further reduction of the *d*-spacing. The ratio of peak height to background (P/B ratio) increased as the AHT temperature increased. The increase of this ratio indicates that the XRD peak sharpened as the temperature increased.

3.4. Thermal stability

Fig. 3 shows the TGA result measured in an inert atmosphere for the untreated and AHT carbon fibers. All the samples exhibited excellent thermal stabilities up to 1000°C. Under close inspection, the thermal stability of the AHT carbon fibers was slightly higher than that of the untreated ones. The commercial PAN-based carbon fibers used presently already have excellent thermal stability, and as such AHT does not increase the stability to any distinguishable degree.

3.5. Single filament tensile properties

The tensile results are shown in Figs. 4-6. As seen in Fig. 4, the single filament tensile strength of the AHT carbon fibers was reduced by about 42-54% from the untreated carbon fiber. This is in agreement with the fact that the tensile strength of PAN-based carbon fiber is normally reduced upon heat-treatment at temperatures higher than 1500°C [1]. The strength reduction was most distinguishable at 1000°C. This is because AHT at high temperatures may cause microstructural defects on the fiber surfaces, leading to a decrease in the mechanical strength.

The tensile modulus of the untreated carbon fiber improved markedly through AHTs as the temperature increased, as demon-

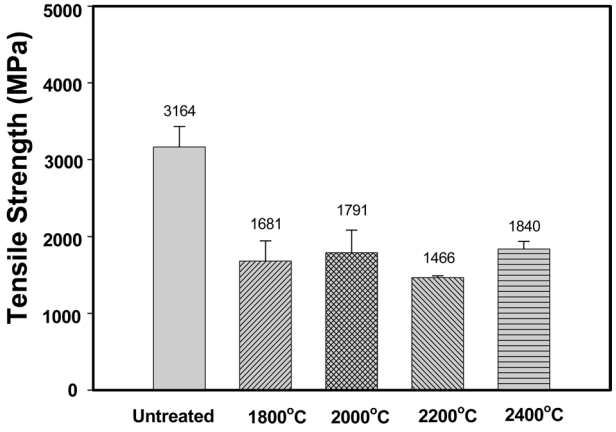

Fig. 4. Variations in the tensile strength measured for polyacrylonitrile-based carbon fibers untreated and additionally heat-treated at different temperatures.

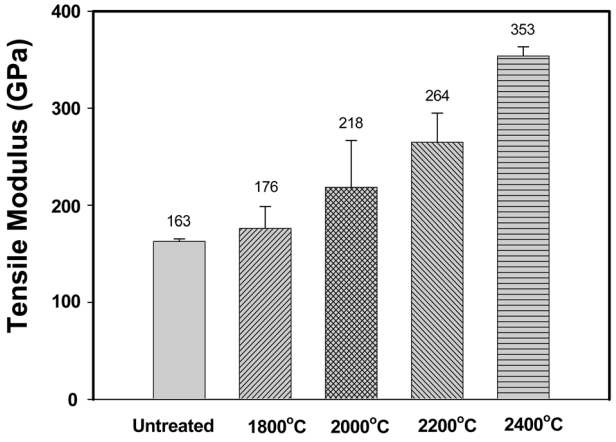

Fig. 5. Variations in the tensile modulus measured for polyacrylonitrile-based carbon fibers untreated and additionally heat-treated at different temperatures.

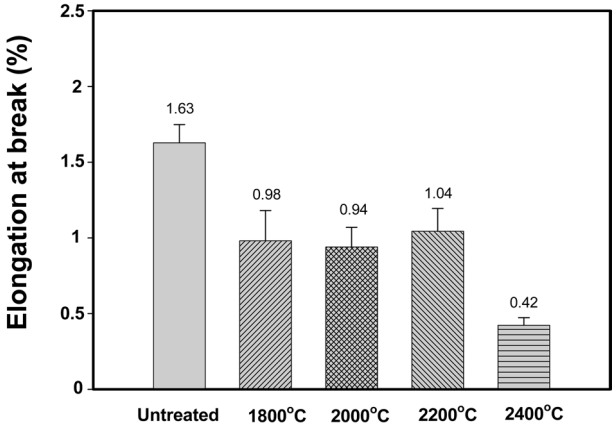

Fig. 6. Variations in the percent elongation at break measured for polyacrylonitrile-based carbon fibers untreated and additionally heat-treated at different temperatures.

strated in Fig. 5. The greatest improvement of about 117% was at 2400°C, over the untreated carbon fiber. This improvement was mainly attributed to the increased molecular orientation along with the fiber direction, leading to increased molecular compaction by the AHT at a graphitization temperature. Such an increase of the tensile modulus was found by extremely high temperature carbonization and/or graphitization of PAN-based carbon fibers with tension in a continuous process. The present result suggests that the tensile modulus of commercial PAN-based carbon fibers can be significantly increased simply through AHT at 2400°C without applying tension in a batch system.

Fig. 6 shows the change of percent elongation at break of the carbon fibers according to the AHT at different temperatures. As expected from the tensile strength and modulus results, the elongation at break decreased according to the degree of AHT received. The most distinguishable reduction of the elongation at break occurred at 1800°C and 2400°C. The elongation 1.63% in the untreated much less than the elongation of 0.42% in the carbon fiber heat-treated at 2400°C, mainly due to the increased tensile modulus, making the carbon fiber stiffer and more brittle.

Table 5. Comparison of the electrical resistivity of PAN-based carbon fibers untreated and additionally heat-treated at different temperatures

Heat-treatment temperature (°C)	Electrical resistivity (μΩ·cm)
Untreated	1699
1800	1098
2000	1040
2200	916
2400	865

PAN: polyacrylonitrile.

3.6. Electrical resistivity

Table 5 summarizes the effect of the AHT temperature on the electrical resistivity of commercial PAN-based carbon fiber. The electrical resistivity was gradually reduced as the heat-treatment temperature increased. The increase in electrical resistivity as the heat-treatment temperature increased was probably due to a crystalline structure change from the relatively-disordered state of the untreated carbon fiber to the ordered state of the AHT carbon fiber although it has a turbostratic structure. The resistivity of 1699 μΩ·cm of the untreated carbon fiber was decreased about 50% to 865 μΩ·cm after AHT at 2400°C, reflecting the increase of the electrical conductivity as well. The resistivity value was similar to that processed at the corresponding heat-treatment temperature of PAN-based carbon fiber [1]. In general, the electrical resistivity of partially or incompletely carbonized fiber is in the range of ~10^4 μΩ·cm or higher. The value increases as the carbonization temperature increases. It was reported that pitch-based carbon fibers with graphitic structures normally exhibit the resistivity of about a few hundred μΩ·cm [1,21]. In fact, the intermediate electrical resistivity between 10^2~10^4 μΩ·cm strongly depends on the heat-treatment conditions used for processing carbon fibers, particularly on the final heat-treatment temperature.

4. Conclusions

As a consequence of investigating the effect of AHT in the temperature range from 1800°C to 2400°C on the chemical composition, morphology, microstructure, single-fiber tensile properties, electrical resistivity, and thermal stability of commercial PAN-based carbon fibers, it has been stressed that commercial PAN-based carbon fiber properties can be further improved upon through AHT without applying tension in a batch process, as drawn in the following conclusions:

1) The carbon content of commercial carbon fibers increased by about 5% by AHT at 2400°C.

2) With increasing AHT temperature, the carbon fiber morphology became uniform and clean, showing the reduction of about 8% in the fiber diameter from 6.82 μm for the untreated carbon fiber to 6.26 μm for the fiber heat-treated at 2400°C.

3) The *d*-spacing gradually decreased with as the AHT temperature increased, whereas the 2θ value was gradually increased. At 2400°C, the *d*-spacing value of carbon fiber was 3.434 Å and the 2θ value was 25.92°.

4) The single-fiber tensile modulus of commercial carbon fibers markedly increased through AHT, in particular showing 117% improvement at 2400°C, whereas both the tensile strength and the elongation at break significantly decreased.

5) The electrical resistivity gradually reduced with increasing AHT temperature, indicating a 50% reduction at 2400°C, compared to the untreated carbon fiber.

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