ICONTECH INTERNATIONAL JOURNAL OF SURVEYS, ENGINEERING, TECHNOLOGY
ISSN 2717-7270
Journal homepage: http://icontechjournal.com/index.php/iij
Volume 5 (2021) Issue 3

CHARACTERIZATION OF CARBON FIBERS DERIVED FROM THERMALLY STABILIZED POLY(HEXAMETHYLENE ADIPAMIDE) PRECURSOR FIBERS

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ABSTRACT

The thermal oxidative stabilization and carbonization processes of poly(hexamethylene adipamide) or (polyamide 66) fibers were accomplished to transform into carbon fibers. Polyamide 66 fibers were pretreated with a ethanol solution of cupric chloride followed by a stabilization process in the air atmosphere. Carbonization experiments were executed at temperatures of 500, 700, 900, and 1100°C utilizing heating rate of 2.5 °C/min. Carbonization experiments were performed at temperatures between 500 and 1100°C employing the rises of 100°C. X-ray diffraction analysis of the carbon fibers shown a highly disordered carbon structure developed during the carbonization process. The values of fiber diameter, linear density, volume density, carbon fiber yield, elemental analysis, and electrical properties revealed a strong dependence on the carbonization temperature. As an insulating material, the polyamide 66 or PA66 precursor was transformed to a semiconducting stage after the thermal stabilization and carbonization processes. The current study demonstrated how processing parameters influence the structure and characteristics of carbon fibers produced from poly(hexamethylene adipamide) fibers.

Keywords: Poly(hexamethylene adipamide), Carbonization, Elemental Analysis X-ray diffraction.

INTRODUCTION

Carbon fiber is a high-performance material containing 92% carbon with the highest specific modulus and specific strength of any reinforcing fiber currently available. Carbon fibers have been utilized as reinforcements in structural composite materials, including carbon fiber-reinforced cement, carbon fiber reinforced polymers, carbon-carbon composites, and carbon fiber reinforced materials for many years (Chand 2000). Electric lights, which Edison invented in 1880 using cellulose-based cotton and bamboo fibers, were the very first industrial implementation of carbon fiber (Edison 1880). In the 1880s, cellulose-based carbon fiber was utilized in the city of Berlin, Germany, for electrical illumination (Frohs and Jaeger 2012). Carbon fibers are produced commercially using a variety of precursors, including PAN (Damodaran, Desai, and Abhiraman 1990), mesophase pitch (Matsumoto 1985), and viscose rayon (Peng et al. 1998).

PAN has become the most widely utilized precursor in carbon fiber synthesis, accounting for around 90% of global carbon fiber production (Liu and Kumar 2012; Yusof and Ismail 2012). High-strength carbon fibers are typically made using PAN fibers; whereas, high-modulus carbon fibers are made with mesophase pitch. Regenerated cellulose-based carbon fibers account for around 1-2 percent of total carbon fiber production worldwide at the moment (Zhang et al. 2006).

Received 7 July 2021; Received in revised form 15 July 2021; Accepted 1 September 2021;
Available online 25 September 2021;
doi: 10.46291/ICONTECHvol5iss3pp48-55

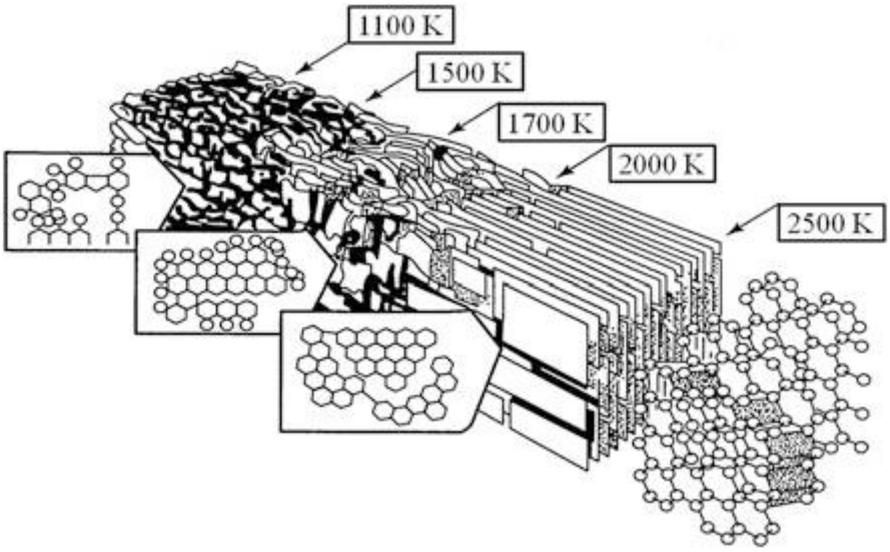
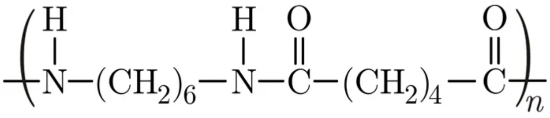


Figure 1: Structural model for carbon fibers during graphitization process (Parker and Waghorne 1982).

Carbon fibers made from cellulose have a lower carbon yield% and have poor mechanical properties, making them impractical for high-strength purposes. Activated carbon fibers are made from cellulose-based precursor fibers (Ko et al. 2002). Activated carbon fibers play an important role in the industrial and medical sectors, including in the water filtration, controlled release of medication supplies, wastewater treatment plants, gas separation for various industrial applications, and so on (Sun, Wu, and Wang 2005). Carbon fibers are typically made by pyrolyzing stabilized precursor fibers under controlled conditions. An oxidization procedure (thermoset treatment) was used to stable and stretch the precursor fibers in air across a temperature range of 200–400°C, which was highly dependent on the natural chemistry of the precursor.



$$-\!\!\left(\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_6-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}\right)_{\!n}\!\!-$$

Figure 2: Chemical structure of Polyamide 66.

The objective of this research was to investigate at the structure and characteristics of carbon fibers made from thermally stabilized polyamide 66 fibers soaked with a ethanol solution of cupric chloride. The impact of processing factors such as carbonization temperature, heating rate, and structural flaws on the fiber characteristics of the resulting carbon fibers were investigated during the experiments.

MATERIALS AND METHODS

To remove surface contaminants from the fibers, the original polyamide 66 multifilaments were treated with a 10% ethanol-water solution at 50°C for 40 minutes. After removing surface contaminants, the sample was allowed to dry at ambient temperature overnight before being dried in an air oven at 80°C for 5 hours. The PA66 yarn was chemically pretreated by soaking it in a solution of 1 percent (w/v) cupric chloride-ethanol for 24 hours at room temperature. The cupric chloride used in this study was bought from Merck (Germany) and utilized without additional purification. The samples were removed from the chemical immersion procedure and dried at 50°C for 24 hours after removing the excess liquid using a cotton cloth. To minimize both yarn shrinkage and disorientation, the chemically treated PA66 yarn was wound around a rectangle shaped stainless steel frame. In the air environment, a two-phase heating technique was used to achieve thermal stability. Utilizing a 1°C/min heating rate, the first heating phase was completed between 175 and 205°C. The following heating step was carried out at 250°C at a rate of 0.3°C/min. The heating time for both stages varied between 0 and 2 hours. To remove the air trapped inside the carbonization oven, a 2 hour purge with a 150 mL/min flow rate was performed prior to the carbonization step. Without any dwell time, carbonization was carried out at temperatures ranging from 500 to 1100°C with 100°C increments. Before extracting the sample from the furnace, a cooling rate of 2°C/min was also

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utilized in this investigation. To analyze and follow the structural variations that happened throughout the carbonization procedures, the values of fiber diameter, linear density, volume density, carbon fiber yield, elemental analysis, X-ray diffraction, and electrical properties were evaluated.

RESULTS AND DISCUSSION

$CuCl_2$ and ethanol solution pretreatment were used to oxidize PA66 fibers in a two-step heating procedure in air. Ethanol was shown to be highly beneficial as a swelling agent for opening up the stiff structure of the PA66 chains by decreasing the interchain forces occurring within hydrogen bonds, allowing cupric ions (Cu^{+2}) to diffuse more quickly into the polymer structure (Pai et al. 1989; Stuart 1994). The first phase in the thermal stabilization process was carried out between room temperature and a temperature range of 175-205°C. Experiments were carried out at temperatures of 175, 190, and 205°C, with dwell times of 0 and 2 hours at every temperature. The second heating phase was set at 250°C for dwell durations ranging from 0 to 2 hours. According to our thermal analysis data (Karacan and Tunçel 2013b, 2013a), a temperature of 250°C is safer to work with in the second step because it is lower than the melting point of PA66 fiber (T_m=258°C). The heating rate was chosen as 1°C/min in the initial stage and 0.3°C/min in the following stage, respectively. The subsequent stage will utilize a slower heating rate (0.3°C/min) to take advantage of the crosslinking processes and examine how they affect the tensile characteristics.

Fiber Diameter

As the temperature of carbonization rises, the diameter values decrease (Figure 3). In comparison to the pure PA66 fiber, the largest diameter reduction was recorded at 1100C, with a loss of roughly 47.2 percent. This significant drop in fiber diameter is thought to be due to the weight loss induced by the removal of volatile compounds in carbonization processes.

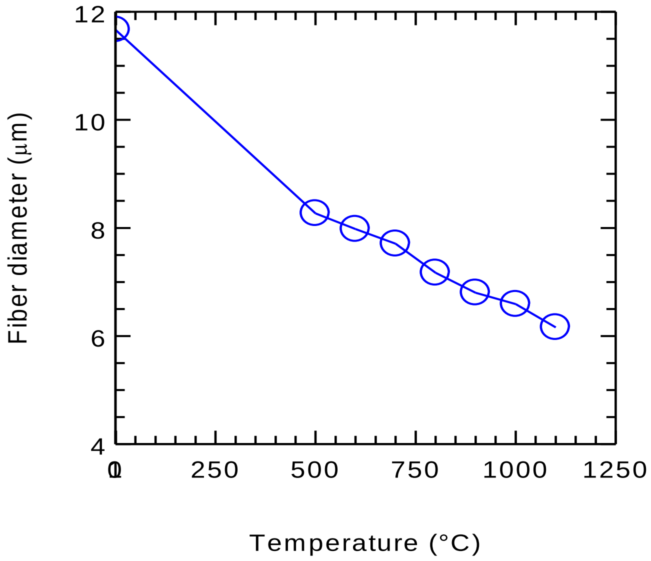

Figure 3: Fiber diameter values of carbon fibers obtained from thermally stabilized PA66 precursor for different carbonization temperatures at the heating rate of 2.5°C/min.

LINEAR DENSITY

The variations in linear density for various carbonization temperatures are illustrated in Figure 4. When the temperature was raised from 500 to 1100°C, the linear density values dropped by 55.9% when compared to the original PA66 fibers. The development of volatiles during the carbonization stage is the primary cause of this massive decrease in linear density.

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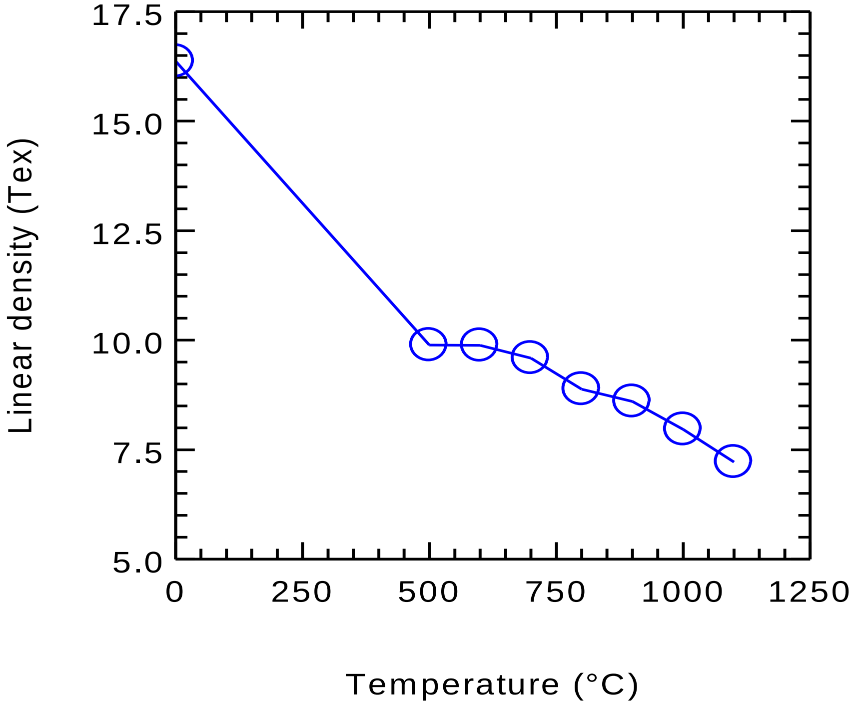

Figure 4: Linear density values of carbon fibers obtained from thermally stabilized PA66 precursor for different carbonization temperatures at the heating rate of 2.5°C/min.

VOLUME DENSITY

The volume densities of carbon fibers for various carbonization temperatures are shown in Figure 5. The values of volume density increased from 1.6176±0.0236 to 1.8643±0.0206 g/cm3 when the temperature was raised from 500 to 1100°C. The widespread development of aromatic structures or large-scale cross-link formations in the carbon fiber structure can be attributed to the significant increase in volume density with increasing temperature. The removal of non-carbon components from carbon fibers due to the creation of heterocyclic rings, as well as the expansion and thickening of aromatic carbon clusters, is attributed to the rise in volume densities caused by rising temperature.

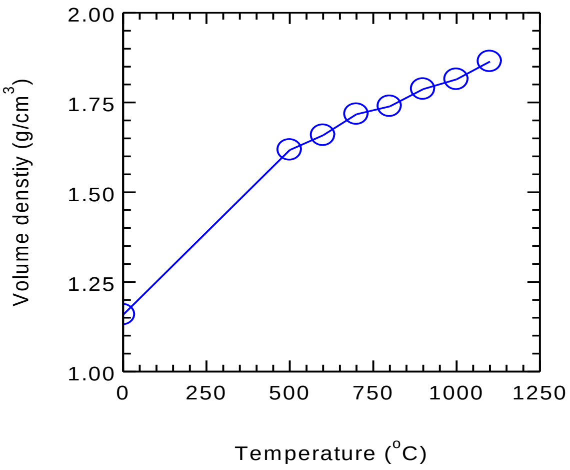

Figure 5 Volume density values of carbon fibers obtained from thermally stabilized PA66 precursor for different carbonization temperatures at the heating rate of 2.5°C/min.

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Elemental Analysis

Figure 6 represents the results of elemental analysis on PA66-based carbon fiber samples. The results show that when the temperature rises, the carbon (percentage) content and the C/H ratio grow, whereas the nitrogen and hydrogen concentration decreases. A considerable percentage of weight is lost during the carbonization process, resulting in a significant amount of volatiles. Although the nitrogen and hydrogen content values drop as the temperature rises, the carbon content tends to rise.

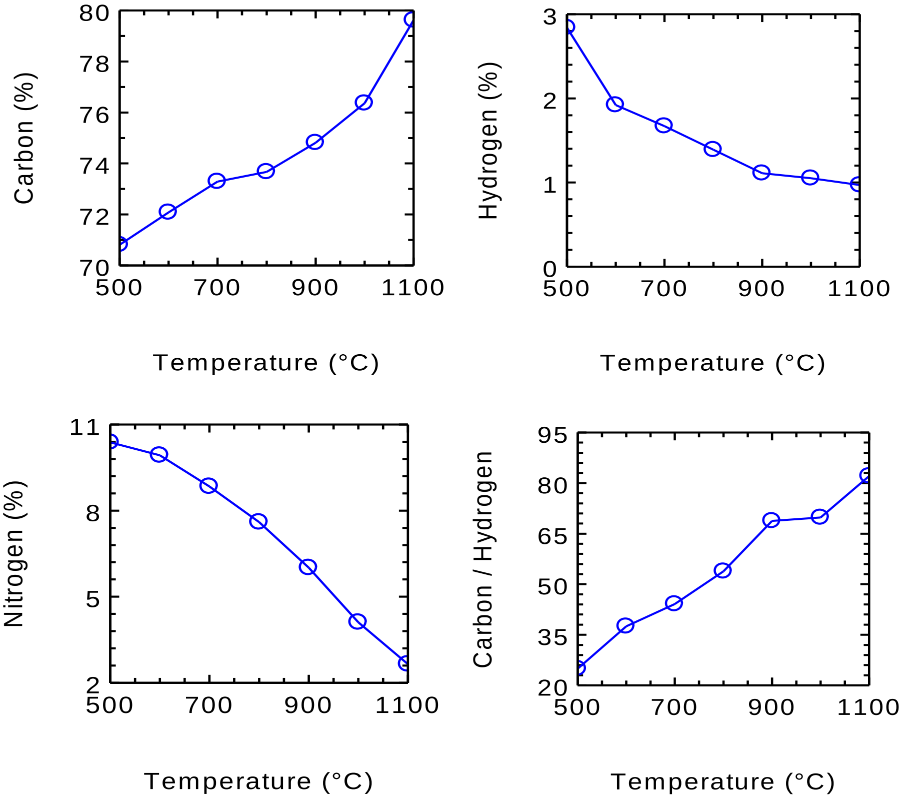

Figure 6: Elemental analysis of PA66-based carbon fibers for different carbonization temperatures.

The carbon content of carbon fiber samples increased gradually from 70.8 to 79.6% when the temperature was raised to 1100°C. The nitrogen and hydrogen levels, on the other hand, gradually decreased to 2.65 and 0.97%, respectively. During the carbonization tests, the increase in carbon content suggests the development of strongly aromatic based carbon clusters. The creation of carbon clusters is predicted to cause the carbon layer planes to reorganize and compress. When the temperature rose between 500 and 1100°C, the carbon-to-hydrogen ratio increased from 24.9 to 82.1% in the carbonization processes.

X-RAY DIFFRACTION

Equatorial X-ray diffraction analysis was used to characterize the structural properties of PA66-derived carbon fibers. In Figure 7, the X-ray diffraction profiles are shown. The development of extremely disordered graphene layers is specified in these diffraction profiles, which were scanned at scattering angles between 10° and 40° 2θ.

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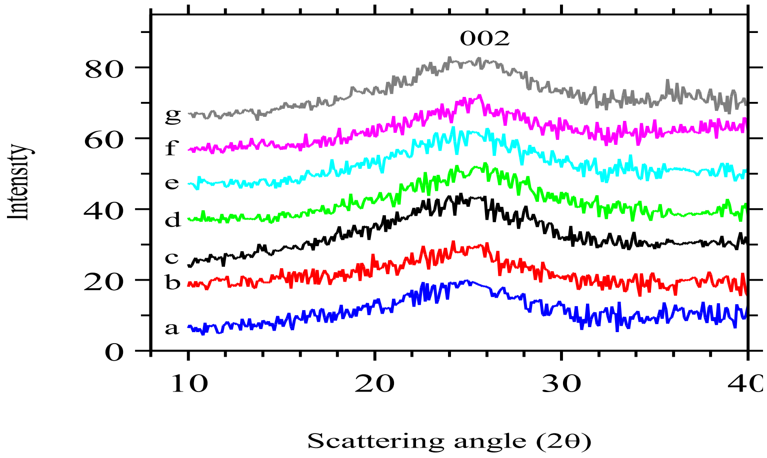

Figure 7: X-ray diffraction profiles of the obtained carbon fibers produced at (a) 500°C, (b) 600°C, (c) 700°C, (d) 800°C, (e) 900°C, (f) 1000°C, and (g) 1100°C.

It is clear that the 2θ position of the (002) reflections increases slightly as scattering angles increase, and the half-height widths narrow slightly as temperature rises, implying that the d-spacing of the (002) reflection decreases and the conforming graphene-like carbon layers (i.e. stacking height) thickens.

ELECTRICAL CONDUCTIVITY

The flow of π-electrons along the fiber axis direction is reported to provide electrical conductivity (Ko and Chen 1999). The electrical conductivity of the original PA66 precursor fiber employed in this work is about 10^{-12} S cm^{-1} (Bajaj, Gupta, and OJHA 2007). The electrical characteristics of carbon fibers are clearly dependent on the carbonization temperature.

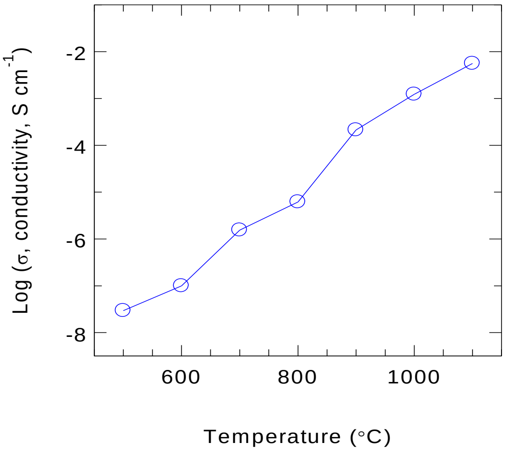

Figure 8: Electrical conductivity of PA66-based carbon fibers for different carbonization temperatures.

Figure 8 depicts the relationship between electrical conductivity and carbonization temperature at room temperature. The carbon content in carbon fibers appears to be increasing due to the removal of non-carbon components such as nitrogen, oxygen, and hydrogen during the carbonization process at 500 to 1100°C, and highly conducting non-graphitizing carbon clusters appear to be generated, resulting in an increase in electrical conductivity. Due to the formation of polyaromatic species and the emergence of hexagonal shaped carbon layers, electrical conductivity was found to be 2.99×10^{-8} S cm^{-1} at 500°C and quickly increases to $5.65\ \times10^{-3}$ S cm^{-1} at 1100°C, i.e. by nearly five orders of magnitude. The findings show that following thermal stabilization and

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carbonization processes, the PA66 precursor fiber, which is a conventional insulator, transforms into a semiconducting material.

CONCLUSION

For the thermal stabilization of PA66 precursor fibers, a two-step stabilization in an air environment was used in this work. The processing parameters had a significant impact on the carbon fibers' tensile properties and volume density values. The carbonization temperature has a significant impact on fiber diameter, linear density, volume density, and tensile characteristics. When carbonized at 1100°C, the PA66 precursor fibers yielded 44% carbon, which is similar to the expected value of 63.7%. The results showed that when the temperature rose, the linear density and fiber diameter values decreased due to the development of volatiles. At temperatures of 500°C and higher, infrared analysis showed the production of highly aromatic carbon clusters. At a temperature of 1100°C, the electrical conductivity of carbon fiber increased to $5.65 \pm 0.04 \times 10^{-3}$ S cm^{-1}. Following the thermal stabilization and carbonization processes, it seems that the PA66 precursor fibers become semi-conducting.

ACKNOWLEDGEMENTS

This study was supported by a grant from the Higher Education Council of Turkey to Md. Mahbubor Rahman.

The first named author Tuba Demirel thanks the Turkish Higher Education Institution YÖK 100/2000 Ph.D. Scholarship Program and the Scientific.

REFERENCES

Bajaj, Priyanshi, A. P. Gupta, and NISHMA OJHA. 2007. “Antistatic and Hydrophilic Synthetic Fibers: A Critique.” *J.M.S.—REV. MACROMOL. CHEM. PHYS.* 40(2&3):105–38.

Chand, S. 2000. “Review Carbon Fibers for Composites.” *Journal of Materials Science* 35(6):1303–13.

Damodaran, S., P. Desai, and A. S. Abhiraman. 1990. “Chemical and Physical Aspects of the Formation of Carbon Fibres from PAN-Based Precursors.” *Journal of the Textile Institute* 81(4):384–420.

Edison, Thomas Alva. 1880. “Electric Lamp.”

Frohs, Wilhelm, and Hubert Jaeger. 2012. “Carbon Fiber & Composite Material–Landscape Germany.” *Carbon* 2(50):737.

Karacan, Ismail, and Kemal Şahin Tunçel. 2013a. “An Assessment of the Impact of Cupric Ion Complexation on Thermal Stabilization of Polyamide 66 as Carbon Fiber Precursor.” *Recent Res. Devel. Appl. Polym. Sci.* 5(1):1–33.

Karacan, Ismail, and Kemal Şahin Tunçel. 2013b. “Thermal Stabilization of Poly (Hexamethylene Adipamide) Fibers in the Presence of Ferric Chloride Prior to Carbonization.” *Polymer Degradation and Stability* 98(9):1869–81.

Ko, Tse-Hao, and Chien-Yuan Chen. 1999. “Improvement in the Properties of PAN-based Carbon Films by Modification with Cobaltous Chloride.” *Journal of Applied Polymer Science* 74(7):1745–51.

Ko, Young Gun, Ung Su Choi, Jeong Su Kim, and Yong Sung Park. 2002. “Novel Synthesis and Characterization of Activated Carbon Fiber and Dye Adsorption Modeling.” *Carbon* 40(14):2661–72.

Liu, Yaodong, and Satish Kumar. 2012. “Recent Progress in Fabrication, Structure, and Properties of Carbon Fibers.” *Polymer Reviews* 52(3):234–58.

Matsumoto, Tadayuki. 1985. “Mesophase Pitch and Its Carbon Fibers.” *Pure and Applied Chemistry* 57(11):1553–62.

Pai, Chih-Chiang, Ru-Jong Jeng, Steven J. Grossman, and Jan-Chan Huang. 1989. “Effects of Moisture on Thermal and Mechanical Properties of Nylon-6, 6.” *Advances in Polymer Technology: Journal of the Polymer Processing Institute* 9(2):157–63.

Parker, B. M., and R. M. Waghorne. 1982. “Surface Pretreatment of Carbon Fibre-Reinforced Composites for Adhesive Bonding.” *Composites* 13(3):280–88.

Received 7 July 2021; Received in revised form 15 July 2021; Accepted 1 September 2021;
Available online 25 September 2021;
doi: 10.46291/ICONTECHvol5iss3pp48-55

Peng, Jimmy C. M., Jean-Baptiste Donnet, Tong Kuan Wang, and S. Rebouillat. 1998. “Surface Treatment of Carbon Fibers.” *Carbon Fibers* 161–229.

Stuart, B. H. 1994. “A Fourier Transform Raman Study of Water Sorption by Nylon 6.” *Polymer Bulletin* 33(6):681–86.

Sun, Junfen, Lishun Wu, and Qingrui Wang. 2005. “Comparison about the Structure and Properties of PAN-based Activated Carbon Hollow Fibers Pretreated with Different Compounds Containing Phosphorus.” *Journal of Applied Polymer Science* 96(2):294–300.

Yusof, N., and A. F. Ismail. 2012. “Post Spinning and Pyrolysis Processes of Polyacrylonitrile (PAN)-Based Carbon Fiber and Activated Carbon Fiber: A Review.” *Journal of Analytical and Applied Pyrolysis* 93:1–13.

Zhang, Huihui, Liwei Guo, Huili Shao, and Xuechao Hu. 2006. “Nano-carbon Black Filled Lyocell Fiber as a Precursor for Carbon Fiber.” *Journal of Applied Polymer Science* 99(1):65–74.

Received 7 July 2021; Received in revised form 15 July 2021; Accepted 1 September 2021;
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doi: 10.46291/ICONTECHvol5iss3pp48-55