DEVELOPMENT OF LOW-COST CARBON FIBERS DERVIED FROM ALBERTA OIL SANDS ASPHALTENE FOR REINFORCING COMPOSITES

Hussain, A*, Bahi, A., Ko, F., and Abdin, Y.
Composites Research Network, Department of Materials Engineering, The University of British Columbia,
Vancouver BC, Canada

* Corresponding author (atif@composites.ubc.ca)

Keywords: *carbon-fiber, sustainability, composites*

ABSTRACT

Carbon fibers are well known for their extraordinary mechanical properties which are beneficial in the production of reinforced composites for high performance applications in aerospace, automotive, civil and sports industries. Carbon fibers are usually expensive and majority of the cost is related to their source. Most of the carbon fibers currently used in industry are derived from polyacrylonitrile (PAN) which is an expensive precursor. Therefore, there is a need to develop low-cost carbon fibers and investigate alternative precursors to meet the future needs of the carbon fiber market. In this study, carbon fibers were synthesized from asphaltene obtained from Alberta Oil Sands. Asphaltenes are a by-product in bitumen processing and can be used as an inexpensive source for carbon fiber production. The fibers were extracted using multiple solvent chemistries and spinning. The fibers then underwent thermal stabilization in air leading to oxidation, cyclization, dehydrogenation, intramolecular crosslinking and aromatization. The fibers were carbonized at high temperatures under nitrogen eliminating impurities and noncarbon atoms. The fiber morphology and diameter were studied using SEM and it was observed that stabilization conditions such as temperature, holding time and heating rate played an important role in defining the fiber structure. The chemical composition of spun fibers, stabilized fibers and carbonized fibers was studied using Fourier Transform Infrared Spectroscopy. The asphaltene based carbon fibers can serve as a low cost alternative route for development of unidirectional carbon fiber reinforced composites using vacuum assisted resin transfer molding process. The asphaltene based carbon fibers show a great potential towards expansion of the carbon fiber commercial market the development of economical low-density high-strength composites for structural and automotive applications.

1 INTRODUCTION

Carbon fibers have been a topic of interest in the field of composites research due to their unique properties including high tensile strength and stiffness, low density, high electrical conductivity, and good flexibility (1,2). These properties of carbon fibers make them an excellent choice of reinforcement material to prepare high performance composites for aeronautics, automobiles, wind and sports industries (3,4).

The global carbon fiber market was estimated at US$ 3.7 billion in 2020, and is expected to reach US$ 6.36 billion by 2025 and US$ 8.9 billion by 2031 (5,6). This anticipated growth is largely due to the automotive sector with an increasing demand in lightweight and fuel-efficient vehicles (7). Currently, the main route of commercial carbon fiber production is via the thermal treatment of fibrous polymer precursors. Their most common precursor is polyacrylonitrile (PAN), while pitch is secondarily used (8). However, the high cost of PAN hampers the widespread use of carbon fibers, since the precursor cost accounts for majority of their production (9). In the recent years, there has been a lot of ongoing research on reducing the overall manufacturing costs of carbon fibers and one of the routes have been utilization of alternative raw materials for precursor development.

Asphaltenes have been rarely researched as a low cost carbon fiber precursor and have been gaining interest in this field. The major applications of asphaltenes are currently in road construction and the building industry. The asphaltene content is usually a measure of the fractions from crude oil based on their solubility in solvents. Asphaltenes are soluble in light aromatics, such as toluene and benzene and insoluble in light alkane/paraffins, such as pentane, hexane or heptane (10).

The structure of asphaltene consists of a polynuclear aromatic core having 4-10 aromatic rings and peripheral aliphatic chains containing 3-7 carbons (11). Stacking of aromatic cores in to aromatic sheets has also been reported (12). Asphaltenes have a high aromatic carbon content (40-50%). Due the chemical composition and structure of asphaltenes as well as their low cost and availability, asphaltenes have a great potential as an alternative precursor for the development of carbon fibers.

The aim is to utilize low cost carbon fibers produced from economical sources, such as asphaltenes for the production of high performance reinforced composites targeting a variety of industries. Research has been conducted on the development of asphaltene based carbon materials, such as carbon nanosheets, foams, fibers, porous carbon and composites that have application in gas adsorption, water purification and electrodes (13,14). The potential of these economical carbon fibers can be further explored to create high value and high performance materials especially for the automotive sector. An example would be to build lighter body frames for electric cars as their batteries are quite heavy contributing to almost 50% of the weight of the vehicle. The reduction in weight would in turn be beneficial for improving the energy efficiency and vehicle performance. Furthermore, the low-cost fibers can be explored for use as functional materials in electromagnetic shields, energy storage devices, supercapacitors and adsorbents (15,16).

Preparation of carbon fibers typically involves steps, such as spinning, thermostabilization, carbonization and graphitization. The main challenge in carbon fiber production using asphaltene precursor is the poor spinnability of asphaltenes. Some studies have reported carbon fiber production using melt spinning process (17). Polymer blending is widely used in the industry to produce suitable precursors for fiber formation and modification of fiber properties (18).

The electrospinning technique is well known for its simplicity and the ability to form fibers in the nano-range. Briefly, the technique produces fibers by applying an electrostatic field between the tip of a syringe that contains the polymer solution and a grounded collector, which stretches the droplets of the polymer solution. The processing parameters (including the feed rate, the solvent, the polymer concentration, the spinning distance, the voltage and the temperature) can be controlled.

This study reports the formation of low cost precursor carbon fibers of asphaltene/PAN fabricated using electrospinning. The thermostabilization and carbonization conditions of the fibers were well investigated and optimized to ensure proper oxidation and maximum yield is achieved. The effect of oxidation temperature on fiber morphology and chemical composition was studied and reported in this paper.

2 MATERIALS AND METHODS

2.1. Materials

Alberta Oil-sands Asphaltene (AOA) was supplied by Alberta Innovates. N, N- Dimethylformamide (DMF, 99.9%), Toluene (98%), Polyacrylonitrile (PAN, M_w = 150 kDalton) were purchased from Aldrich.

2.2. Electrospinning of AOA based carbon fiber

AOA sample was used as obtained without any further purification. AOA and PAN were dissolved in the solvents, toluene and DMF, at different weight ratios. The solution was heated at 60-80 °C for 2 hours, undergoing vortexing for few seconds at 30 min intervals. The temperature was controlled and kept at approximately 15°C during this process using ice in the water bath. Later, the ice was removed to keep the temperature in the desired range.

Electrospinning of fiber mats (Figure 1) was carried out in a horizontal orientation using a 10mL syringe fitted in a 25 G needle with a nanofibre electrospinning unit (Kato Tech Co. Ltd., Kyoto, Japan). The operating voltage was kept constant at 15-20 kV, syringe pump flow rate was at 0.1 mm/min, and spinning distance was at 15-18 cm.

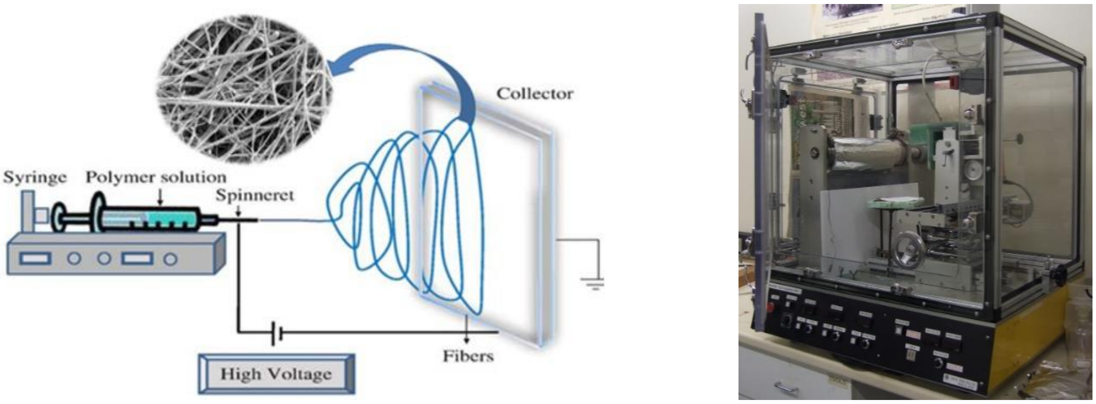


Figure 1. Electrospinning set-up: schematic diagram (left), and the actual unit (right) (19).

2.3. Fiber thermostabilization and carbonization: process and parameters

A tube furnace (MTI Corp, Richmond, CA, USA) was used for thermal treatment of the electrospun AOA-based nanofibers from 25 °C to 200-300 °C at a rate of 0.5 °C/min and held constant for 60 min in air. Subsequently, the thermostabilized fibers were heated in nitrogen atmosphere at 5 °C/min up to 1000 °C and held constant for 60 min.

2.4. Characterization of the AOA based carbon fibers

The morphology of the electrospun nanofibrous mats was observed by a scanning electron microscope (SEM) model S-2300 (Hitachi Ltd., Tokyo, Japan) with an acceleration voltage of 5-20 kV. All of the samples were gold coated prior to SEM observation. The average diameter of nanofibers was determined by analyzing the SEM images via Image J software.

Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer Model Q500 (TA Instruments, Newcastle, DE, USA). Samples were heated using the fiber thermostabilization and carbonization conditions (mentioned in Section 2.3) and the yield was determined from the mass loss curves.

Differential scanning Calorimetry was performed on the samples using a DSC Model 2500 Discovery (TA Instruments, Newcastle, DE, USA). The samples were heated at 4 °C/min from 25 °C - 400 °C in an inert atmosphere.

The presence of characteristic absorption bands was studied by ATR-FTIR spectroscopy Model FT-660 (Agilent Technologies, CA, USA) using a crystal diamond accessory. Transmittance spectra were recorded for a wavelength range from 4000 to 600 cm^{-1}. A total of 64 scans were taken, and the resolution was set to 4 cm^{-1}.

3 RESULTS AND DISCUSSION

3.1. Thermal treatment process for stabilization and carbonization

A differential scanning calorimeter was used to determine the crosslinking temperature of the AOA-PAN fibers was determined. As seen in Figure 2, a strong exothermic peak, associated with crosslinking reactions, aromatization and inter-molecular and intra-molecular cyclization, was observed at 287 °C for the electrospun AOA-PAN fibers. The thermal process that converts the usual PAN based fibers into carbon fibers is characterized by three main steps: thermostabilization/oxidation, high temperature carbonization and graphitization.

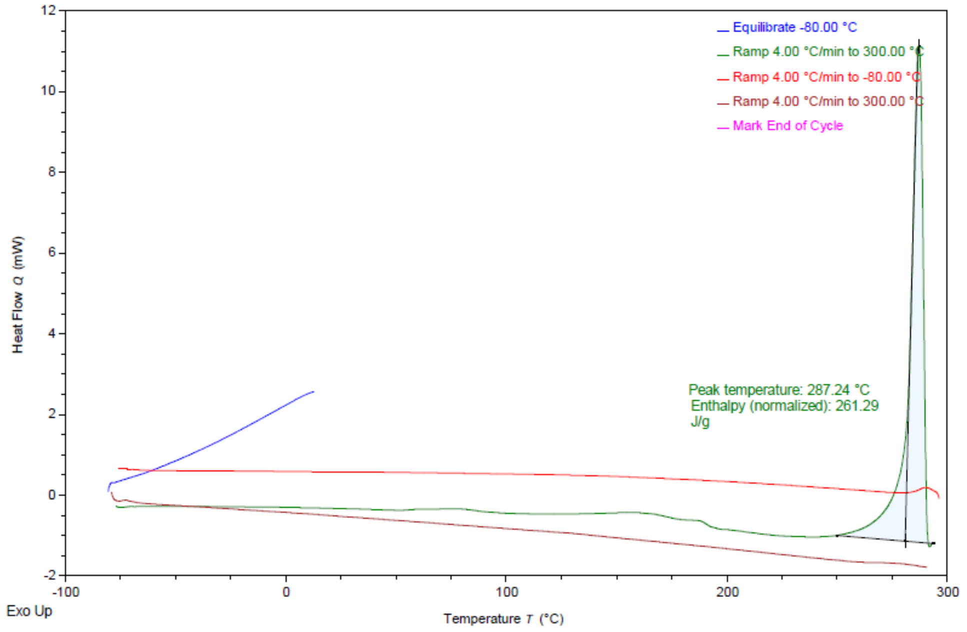


Figure 2. DSC curve of electrsopun fibers.

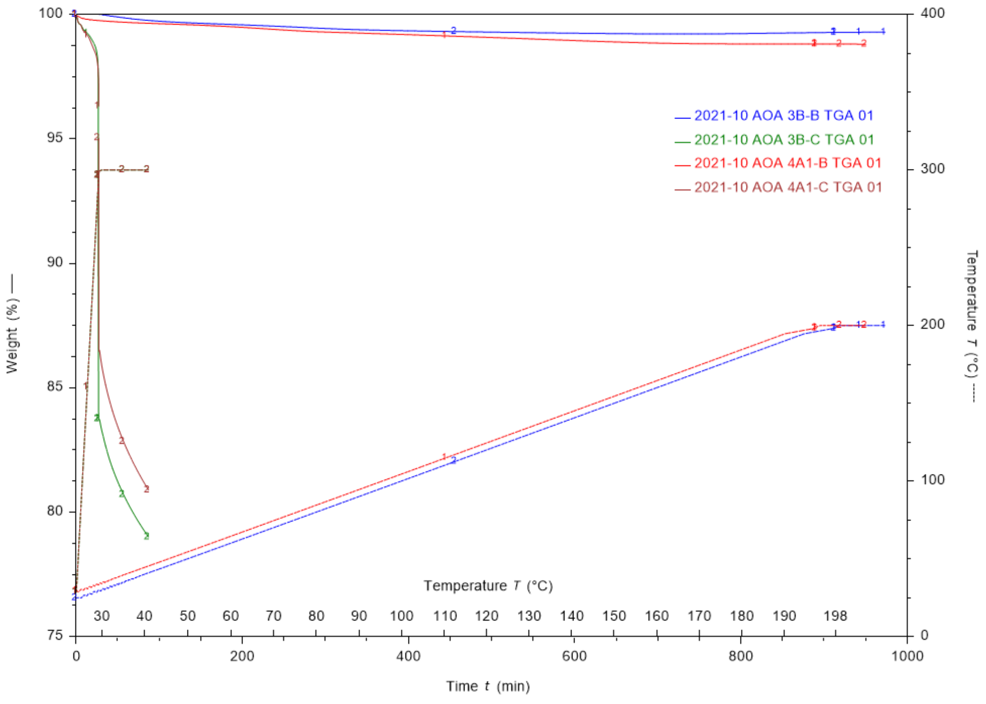
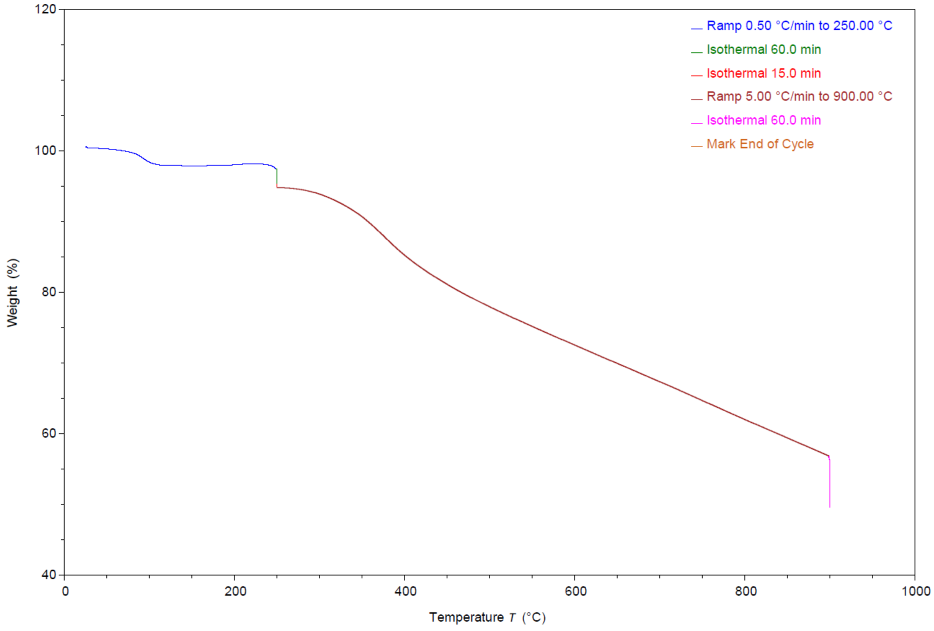


Figure 3. Thermal stabilization of electrospun fibers using TGA.



TA Instruments Trios V5.0.0.44616

Figure 4. Thermostabilization and carbonization of electrospun precursor fibers

The thermal treatment process involves two steps in general: Thermostabilization of precursor fibers at temperatures of 200 – 300 °C performed in air followed by carbonization under an inert atmosphere at temperatures higher than 600 °C.

The thermostabilization step plays an important role in the formation of a ladder structure which further allows processing of the stabilized fibers at higher temperatures without fusing or melting. In our study, the thermostabilization was performed at different temperatures: 200, 250 and 300 °C. From the TGA results (Figures 3 and 4), it was observed the the fibers do not undergo significant mass loss when the thermostabilization step is performed at 200 and 250 °C. However, as the temperature was increased to 300 °C for the thermostabilization step, almost 20% mass loss was observed.

During the thermostabilization step, it has been reported that oxygen promotes inter and intramolecular reaction, supporting intramolecular crosslink and aromatization. Oxygen is not directly involved in cyclization, but it supports the dehydrogenation of the main carbon chain. Various structures containing oxygen have been proposed, in which oxygen was involved in ether bridges, carbonyl groups or interacting with the nitrogen, through donation of the lone pair from nitrogen to oxygen atom. Also, intermolecular reactions such as the formation of azomethine and nitrile crosslinks have been suggested (20).

Following the thermostabilization step, the oxidized fibers were then exposed to higher temperatures up to 1000 °C in a nitrogen atmosphere. It was seen that the stabilized fibers underwent 40% mass loss during the carbonization step as observed in the TGA results (Figure 4). The carbonization steps involves removal of noncarbon atoms such as oxygen, nitrogen and hydrogen and formation of carbon char. The formation of a condensed aromatic ring has been reported during the carbonization step, which takes place through the condensation of ladder structures. Furthermore, the elimination of almost all oxygen atoms in the form of CO and CO_2, most of the nitrogen as HCN and NH_3, and some removal of carbon as oligomers is expected to take place during the carbonization step (21).

3.4. Chemical Characterization

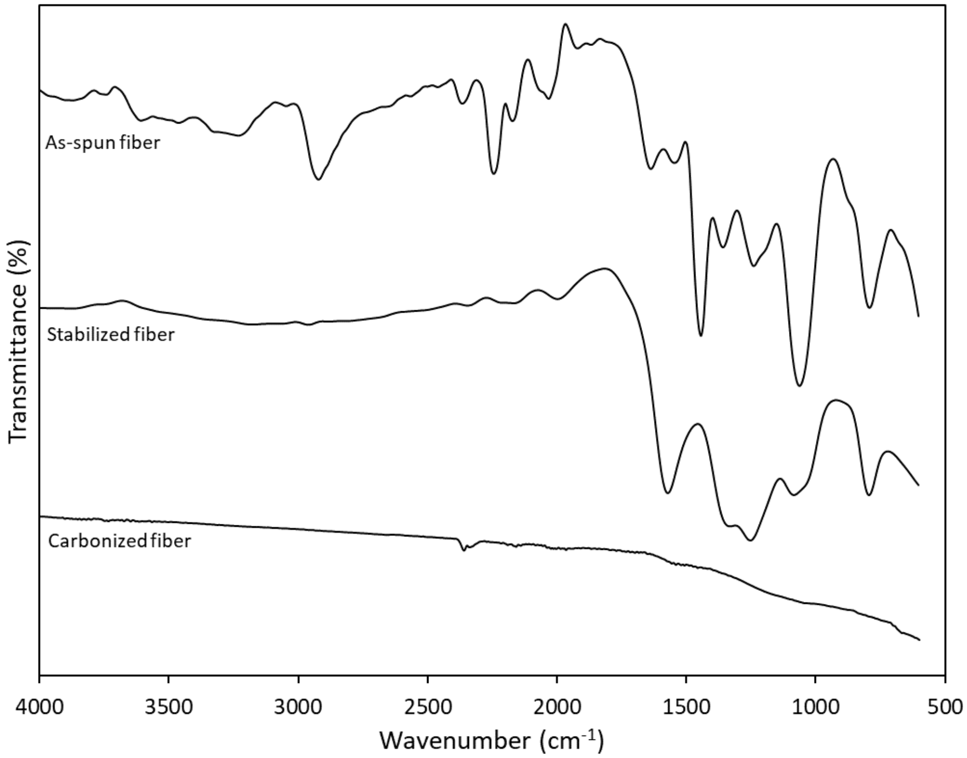


Figure 5. FTIR spectra of electrospun carbon fibers before and after undergoing thermal treatment.

Table 1. FTIR peak analysis of the electrospun fibers.

Wavenumber (cm^{-1})	**Assignments**	**Samples**
2850-2930	Aliphatic CH stretching	As spun
2241	CN symmetric stretching	As spun
1641, 1653	C=O stretching	As spun
1565	C=C and C=N stretching	Stabilized
1440	Aliphatic CH bending	As spun
1253	CH wagging	As spun, stabilized
~1100	C-O-C	Stabilized
1026, 1067, 1085	C-C stretching, C-CN combination mode	As spun, stabilized
780	triazine ring	As spun, stabilized

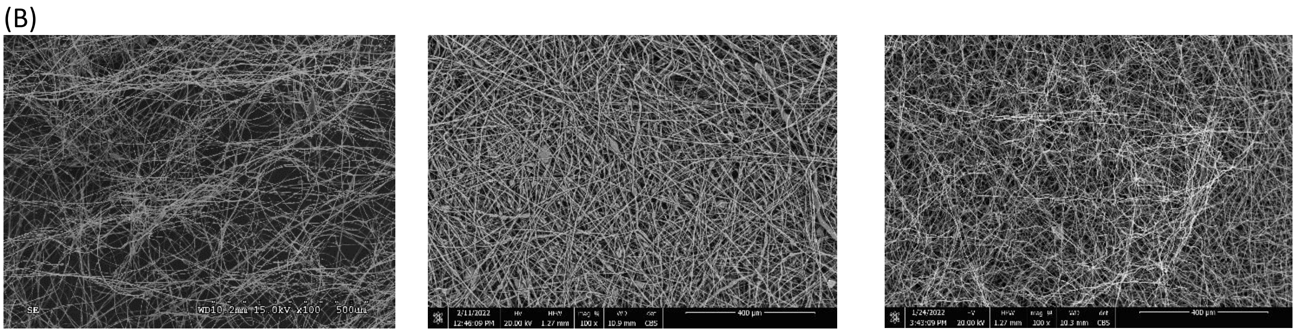
The as-spun, thermostabilized and carbonized samples were characterized for their chemical bonds using FTIR analysis. The peaks corresponding to the respective bonds are presented in Table 1.

As seen in Figure 5, stabilized fibers have a new peak around 1560 cm-1 corresponding to C=O bonds showing that oxidation has taken place in these fibers. The peak corresponding to this region indicates presence of carboxyl, carbonyl, ether and ester and ketone bonds that have been formed due to the oxidation of fibers during the after thermostabilization step. On the other hand, peaks corresponding the aliphatic CH stretching at 2923 and 2852 cm^{-1} as well as the peak at 1452 cm^{-1} corresponding to the aliphatic C-H bending have disappeared in the stabilized samples which are also an indication of good oxidation conditions (21,22).

As seen in the Table 1, the peaks corresponding to presence of ketones and polyaromatics groups indicate that dehydration and cyclization reactions have occurred during the thermostabilization step. For the carbonized sample, majority of the peaks disappeared indicating elimination of all the functional groups. During the carbonization step, there is the formation of condensed aromatic ring, through the condensation of a series of ladder structures. This step is accompanied by the elimination of almost all nitrogen as HCN and NH_3, of oxygen atoms as CO and CO_2, and a minor elimination of carbon as oligomers (23).

3.3. Morphological results from SEM data

As spun Stabilized Carbonized



As spun Stabilized Carbonized

Figure 6. (A) Photographs of the produced carbon fiber mats; (B) SEM micrographs of the carbon fiber mats.

In order to retain fiber shape during carbonization, electrospun fibers usually undergo thermal or thermal-oxidative stabilization by heating samples at controlled rates to specific temperatures as described in the previous sections. This process when well optimize, was also expected to be the one of the methods to enhance higher yield of carbon.

The samples here in were thermally oxidatively stabilized and the resulting samples were analyzed for fiber size. The morphology of the samples, as well as fiber diameter appear to be dependent upon stabilization parameters, especially on final temperature. As shown in Fig.6, good uniform fibers were obtained from electrospinning of asphaltene under optimal conditions. The thermostabilization temperature played a major role in obtaining good yield of carbonized fibers without fusing or melting at higher temperatures. As observed under the SEM, the average fiber diameter was around 700-800 nm.

4 Conclusions

In this study, successful production of carbon fibers from asphaltene, obtained from Alberta Oil Sands, has been demonstrated using the electrospinning method. The thermal treatment of fibers was investigated and the thermostabilization and carbonization parameters were optimized using TGA. Morphological examination of the stabilized and carbonized fibers showed individual uniform fibers having a relatively good length without any obvious defects. The average diameter of the fibers was found to be in the nano-range, which is possible due to the electrospinning fiber manufacturing process. The chemical characterization of stabilized fibers clearly showed the presence of oxygen containing functional groups which are absent in the as-spun fibers indication successful oxidation during the thermostabilization step. The fibers were seen to have a good yield after carbonization at 1000 °C and the quality of the carbonized mats are acceptable to be further used in the resin infusion process for development of composites.

References

1. Forintos N, Czigany T. Multifunctional application of carbon fiber reinforced polymer composites: Electrical properties of the reinforcing carbon fibers – A short review. Vol. 162, Composites Part B: Engineering. Elsevier Ltd; 2019. p. 331–43.
2. Yao SS, Jin FL, Rhee KY, Hui D, Park SJ. Recent advances in carbon-fiber-reinforced thermoplastic composites: A review. Vol. 142, Composites Part B: Engineering. Elsevier Ltd; 2018. p. 241–50.
3. Yang XD, Gu F, Chen X. Performance Improvement of Carbon Fiber Reinforced Epoxy Composite Sports Equipment. In: Key Engineering Materials. Trans Tech Publ; 2021. p. 228–33.
4. Das TK, Ghosh P, Das NCh. Preparation, development, outcomes, and application versatility of carbon fiber-based polymer composites: a review. Advanced Composites and Hybrid Materials [Internet]. 2019;2(2):214–33. Available from: https://doi.org/10.1007/s42114-018-0072-z
5. https://www.marketsandmarkets.com/Market-Reports/carbon-fiber-396.html [Internet]. 2021 [cited 2021 Dec 1]. Available from: https://www.marketsandmarkets.com/Market-Reports/carbon-fiber-396.html
6. https://www.grandviewresearch.com/press-release/global-carbon-fiber-market [Internet]. [cited 2021 Dec 1]. Available from: https://www.grandviewresearch.com/press-release/global-carbon-fiber-market
7. Ahmad H, Markina AA, Porotnikov M v., Ahmad F. A review of carbon fiber materials in automotive industry. In: IOP Conference Series: Materials Science and Engineering. IOP Publishing Ltd; 2020.

8. Khayyam H, Jazar RN, Nunna S, Golkarnarenji G, Badii K, Fakhrhoseini SM, et al. PAN precursor fabrication, applications and thermal stabilization process in carbon fiber production: Experimental and mathematical modelling. Vol. 107, Progress in Materials Science. Elsevier Ltd; 2020.
9. Warren CD, Paulauskas FL, Baker FS, Eberle CC, Naskar A. Development of commodity grade, lower cost carbon fiber-commercial applications. SAMPE J. 2009;45(2):24–36.
10. Acevedo S, Escobar O, Echevarria L, Gutiérrez LB, Méndez B. Structural Analysis of Soluble and Insoluble Fractions of Asphaltenes Isolated Using the PNP Method. Relation between Asphaltene Structure and Solubility. Energy & Fuels [Internet]. 2004 Mar 1;18(2):305–11. Available from: https://doi.org/10.1021/ef030065y
11. Kim JG, Kim JH, Song B-J, Lee CW, Im JS. Synthesis and its characterization of pitch from pyrolyzed fuel oil (PFO). Journal of Industrial and Engineering Chemistry [Internet]. 2016;36:293–7. Available from: https://www.sciencedirect.com/science/article/pii/S1226086X16000769
12. da Costa LM, Stoyanov SR, Gusarov S, Tan X, Gray MR, Stryker JM, et al. Density Functional Theory Investigation of the Contributions of π–π Stacking and Hydrogen-Bonding Interactions to the Aggregation of Model Asphaltene Compounds. Energy & Fuels [Internet]. 2012 May 17;26(5):2727–35. Available from: https://doi.org/10.1021/ef202010p
13. Qin F, Jiang W, Ni G, Wang J, Zuo P, Qu S, et al. From Coal-Heavy Oil Co-refining Residue to Asphaltene-Based Functional Carbon Materials. ACS Sustainable Chemistry and Engineering. 2019 Feb 18;7(4):4523–31.
14. Kueh B, Kapsi M, Veziri CM, Athanasekou C, Pilatos G, Reddy KSK, et al. Asphaltene-Derived Activated Carbon and Carbon Nanotube Membranes for CO2 Separation. Energy and Fuels. 2018 Nov 15;32(11):11718–30.
15. He M, Xu P, Zhang Y, Liu K, Yang X. Phthalocyanine nanowires@ GO/carbon fiber composites with enhanced interfacial properties and electromagnetic interference shielding performance. Chemical Engineering Journal. 2020;388:124255.
16. Liu H, Xu T, Liu K, Zhang M, Liu W, Li H, et al. Lignin-based electrodes for energy storage application. Industrial Crops and Products [Internet]. 2021;165:113425. Available from: https://www.sciencedirect.com/science/article/pii/S0926669021001898
17. Zuo P, Leistenschneider D, Kim Y, Abedi Z, Ivey DG, Zhang X, et al. Asphaltene thermal treatment and optimization of oxidation conditions of low-cost asphaltene-derived carbon fibers. Journal of Industrial and Engineering Chemistry. 2021 Dec 25;104:427–36.
18. Culebras M, Beaucamp A, Wang Y, Clauss MM, Frank E, Collins MN. Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors. ACS Sustainable Chemistry and Engineering. 2018;6(7):8816–25.
19. Faki R, Gursoy O, Yilmaz Y. Effect of Electrospinning Process on Total Antioxidant Activity of Electrospun Nanofibers Containing Grape Seed Extract. Open Chemistry. 2019;17(1).
20. Wu M, Wang Q, Li K, Wu Y, Liu H. Optimization of stabilization conditions for electrospun polyacrylonitrile nanofibers. Polymer Degradation and Stability. 2012 Aug;97(8):1511–9.
21. Cipriani E, Zanetti M, Bracco P, Brunella V, Luda MP, Costa L. Crosslinking and carbonization processes in PAN films and nanofibers. Polymer Degradation and Stability. 2016 Jan 1;123:178–88.
22. Coleman MM, Petcavich RJ. Fourier transform infrared studies on the thermal degradation of polyacrylonitrile. Journal of Polymer Science: Polymer Physics Edition. 1978 May;16(5):821–32.
23. Xue TJ, Mckinney MA, Wilkie CA. The thermal degradation of polyacrylonitrile.