EFFECT OF HEAT TREATMENT ON POROSITY IN ASPHALTENE-DERIVED CARBON FIBERS

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ABSTRACT

Asphaltenes are complex mixtures of aromatic organic compounds present in petroleum and coal. Due to the low cost of Alberta oil sands asphaltenes (AOAs), they have been studied as alternate materials to polyacrylonitrile (PAN) as precursors for carbon fibers used in applications where excellent mechanical properties are not required, such as porous carbon fibres. Porous carbon fibers have potential applications as activated carbon fibers used in separation, purification, and catalysis processes.

This work investigates the formation of microporosities in AOAs-derived carbon fibers in response to temperature treatments and attempts to ascertain the mechanism by which the porosities are formed. Melt-spinning was used to convert the as-received AOA powder into fibrous form. The as-received asphaltenes and derived carbon fibres were characterized using differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and elemental analysis (EA) to understand the effect of heat treatment on the material composition and properties. The microstructure and crystallinity of the carbon fibres were examined using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The formation of microporosity was not correlated to the volatilization of heteroatoms like sulfur, nor the removal of organic side chain groups, as originally hypothesized. Instead, imperfect stabilization is a more likely reason for the formation of voids in AOA-derived carbon fibers. Further investigations are required to analyze the pore structures formed.

1 INTRODUCTION

Asphaltenes, derived from oilsands or coal, possess significant potential as low-cost feedstocks for synthesizing and developing functional carbonaceous materials due to their high carbon content, aromaticity, and double bond equivalents (DBE). It has been demonstrated by Saad et al. [1] that asphaltenes are suitable precursors for melt-spinning fibres due to their favourable shear viscosity properties. Saad et al. [1] produced carbon fibres from asphaltenes with an average tensile strength of ~400 MPa and an average elastic modulus of ~70 GPa, by carbonizing their AOAs fibers at relatively low temperatures of 500°C and 800°C [1]. In polyacrylonitrile (PAN) and pitch-derived carbon fibers, the mechanical properties of the carbon fibers are generally reported to increase with higher temperature treatment due to the growth and coalescence of the graphitic regions. Therefore, barring other reactions, increasing the carbonization temperature would be expected to enhance the tensile strength and modulus of AOA-derived fibers. However, high temperature (>1000 °C) treatment was found to decrease strength and stiffness in our work. Scanning electron microscopy revealed the presence of voids and micro voids, which act as stress concentrators and reduce the mechanical properties of the AOA-derived carbon fibers that were treated at high temperatures (>1000 °C). In this work, we investigate the effect of temperature treatment on the presence of voids in the carbon fibers. The motivation for this study is to understand if AOA-derived fibers would be well-suited as low-cost precursors for porous carbon fibers to complement current research on asphaltene-derived isotropic carbon fibers. Porous carbon fibers have applications in energy conversion and storage, biomedical engineering, adsorption and filtration, purification, catalysis, and chemical detection and sensing [1]. Currently, porous fibers are made by sacrificial particle etching, phase separation, low melting point metal (zinc) evaporation, gas foaming, electrochemical oxidization, and crazing [1].

With respect to AOA-derived carbon fibers, we hypothesized that high-temperature treatment might result in the formation of pores and micropores by means of two mechanisms. Firstly, AOAs contain relatively high levels of heteroatoms, such as sulphur (7-8%) and nitrogen (1-2%), compared to PAN and pitch. These compounds may volatilize during high-temperature treatment, potentially leaving behind microporosity. Secondly, literature reports that AOAs contain high amounts of low-temperature (<500 °C) volatiles, which may degrade or volatize and thus leave behind porosity.

In this study, we investigate the effect of carbonization temperatures on the porosity of the obtained carbon fibers. Asphaltenes were melt-spun, stabilized by chemical and thermal treatment, and carbonized in an inert atmosphere. The development of microporosity in the carbon fibers was demonstrated through microscopic imaging. Elemental analysis was utilized to measure the concentration of heteroatoms in the resultant carbon fiber asphaltenes.

2 Experimental

2.1 Materials and Fiber Fabrication

The AOAs sample labelled as S1 was supplied by Alberta Innovates and used as received. Concentrated HNO_3 (70%, reagent, certified ACS plus) was procured from Thermo Fisher Scientific and diluted with reverse-osmosis water. The melt-spinning process was completed using a custom-built melt spinner with a spinneret hole with a diameter of 1 mm. A weight of 250 grams was applied to the material through the small inlet located at the top of the chamber to help the material form a droplet, which was pulled and then collected in a fibrous form on a rotating drum. The rotation speed of the drum progressively increased from 0 to 100 m/min and then held at 100 m/min steady state conditions. The melt-spinning temperature for the S1 as-received asphaltenes was selected to be 220°C (40°C above the softening point) [1]. The asphaltene fibers were dipped into 20 vol% (3.16 M) HNO_3 and kept in solution for 10 minutes. The fibers were stabilized by heating from room temperature to 250°C in a tube furnace (Carbolite Gero Corporation) equipped with an alumina tube for 6 hours with a heating rate of 2.5°C min^{-1} under a flowing laboratory air atmosphere with the airflow of 60 ml/min. The fiber sample was cooled at the same rate after this oxidative stabilization process. Fibers were carbonized at 500°C, 800°C and 1000 °C for a 1-hour soaking time at each temperature with a heating rate of 1.5 °C/min in a vacuum environment with a vacuum pressure of 0.05 mbar.

2.2 Characterization

The thermal stability of AOAs was analyzed via thermogravimetric analysis (TGA) using a Discovery TGA 550 analyzer (TA Instruments, USA). Measurements were done in the temperature range from 20 to 800 °C with a heating rate of 10 °C/min under nitrogen and air atmospheres. Differential scanning calorimetry (DSC) was used to investigate any glass transition temperatures (T_g) and melting temperatures (T_m). DSC analysis of samples was conducted using a Mettler Toledo DSC 3+ model under a nitrogen atmosphere with a heating and cooling rate of 10 °C/min. The rheological properties of the S1 asphaltenes were analyzed using an Anton Paar modular compact MCR 302 rheometer at various temperatures in an inert N_2 atmosphere. Measurement was conducted at a 1 mm gap height utilizing a 25 mm aluminum parallel plate setup with a disposable bottom cup. The temperature-controlled measurement started once the oven's temperature stabilized within ±0.5 °C for 180 seconds to prevent temperature variations. A high-temperature gas chromatograph (GC-2010, Shimadzu, Japan) simulated distillations (SimDist) GC-FID analysis with a dual flame ionization detector following ASTM 7169 standard was used to analyze the boiling point distribution of as-received asphaltenes. The CHNS composition study was conducted using Elementar Unicube Elemental Analyzer equipment. Samples were finely ground in an agate mortar before the measurement and weighed into tin crucibles. An Agilent Fourier Transform Infrared Spectrometer (Agilent Cary 630 Fourier) was utilized to compare the spectrums after each thermal treatment stage. The samples underwent analysis within the 400 to 4000 cm^{-1} spectral region with an average of 128 scans under normal room temperature conditions. To ensure the data's repeatability, every sample was examined twice. The powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 Advance ECO diffractometer equipped with a Cu Ka source with the wavelength 1.54178 Å, working with the voltage of 40 KV, and a current of 25 mA and an LYNXEYE XE detector. The samples were loaded into a 25 mm PMMA sample holder, and the experimental data was collected from 5-70° 2θ at a 1.2°/min scan rate. The fibers' surface morphologies, cross-section, and size were examined using a field emission scanning electron microscope (FEI Quanta 250 FEG).

3 Results and Discussion

3.1 Characterization of as-received S1 asphaltenes

The DSC data presented in Figure 1a shows an endothermic reaction around 75 °C in the first cycle. This signal can be attributed to evaporating water or other molecules with low molecular weight. According to the asphaltene sample bank datasheet provided by Alberta Innovates, as-received asphaltenes may contain residual water and solvent from extracting it from bituminous oilsands. This interpretation is supported by the differential thermogravimetric (DTG) curve displayed in Figure 1b, which shows mass loss at the same temperature. No clearly defined melting point can be observed in the DSC curve, indicating that as-received asphaltenes were amorphous in nature. The TGA results (Figure 1b) indicate that at melt-spinning and thermal stabilization temperatures (220 °C and 250 °C, respectively), the as-received S1 asphaltenes underwent around 2.5 wt % weight loss. The emission of volatile compounds takes place within two defined temperature ranges, denoted as volatiles 1 and 2 on the curve shown in Figure 1b. Volatiles in the temperature range of 20−350 °C are ascribed to hydrocarbons with low boiling points [2]. The primary weight loss, denoted as Volatiles 2, takes place within the temperature range of 350−500 °C. This weight loss is caused by the breakdown of the weaker bonds, which are not part of the primary aromatic systems, such as side chain groups that vaporize within the specified temperature range [2]. The TGA curve obtained in an inert N_2 atmosphere at the temperature of 800 °C provides information about the proportion of solid carbon residue that remains after the volatile components have been removed, which equals ~30 wt % of the initial weight.

Figure 1c shows the viscosity versus temperature of as-received S1 asphaltenes. Based on the literature, the suitable viscosity range to maintain an ideal flow for smooth and continuous extrusion of fibers is found to be in the range of 20 and 70 Pa.s [1]. To operate within this viscosity range, the melt-spinning temperature was varied between 220° and 245°C with an interval of 10°C. However, it was observed experimentally that at 245°C, the S1 sample showed too low viscosity; thus, melt-spinning was not feasible at that temperature. SimDist GC-FID results are presented in Figure 1d. The x-axis represents the boiling point range of hydrocarbons. This distribution helps in determining which components of asphaltenes boil off at specific temperatures. Each peak represents a different hydrocarbon or fraction, with the area under the peak corresponding to the concentration of that fraction. In complex mixtures like asphaltenes, these peaks can provide insights into the presence of light, medium, heavy, and very heavy fractions. As indicated, the majority of the molecules in S1 are found in the initial third set (C1-C34) of the fractions. Fractions with low boiling points (C1-C17) may cause gas bubble formation during spinning. Additionally, it was noted that the sample contained a significant amount of large molecules with high boiling points, as indicated by the increased proportion of these molecules at the higher temperature ranges (C98-C100) and are likely beyond the measurement range of the machine.

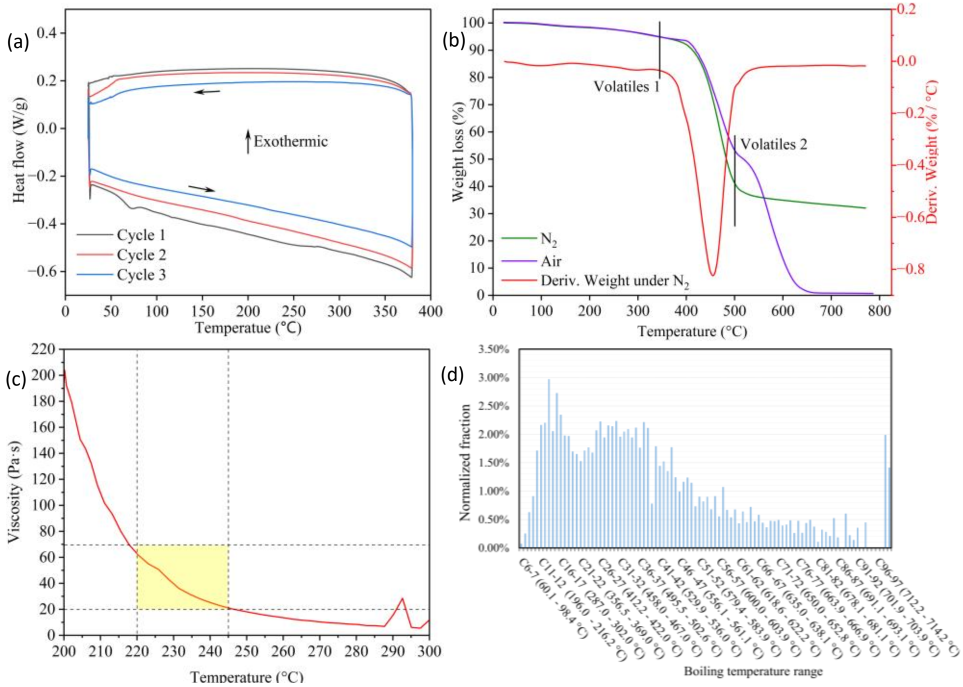

Figure 1. (a) DSC analysis under nitrogen, (b) TGA and DTG curves under nitrogen and air, (c) viscosity versus temperature data, (d) Sim-Dist GC-FID of as-received S1 asphaltenes.

3.2 Characterization of asphaltene-derived fibers

Figure 2a shows a representative of melt-spun asphaltene fibers. In the nitric acid-treated fibers, it was observed that nitric acid did not have a disruptive effect (i.e., causing etching) on the spun fibers' surface at the soaking time and acid concentration used. Figure 2b shows fibers carbonized at 500°C for 1 hour without any visible porosities or surface degradation. Porosities, appearing as surface defects, emerged when fibers were subjected to a higher temperature at 800 °C for 1 hour, as represented in Figure 2c, showing evident surface damage. The porosities grew in size and number when the fibers were carbonized at 1000 °C for 1 hour, as shown in Figure 2d.

FTIR was utilized to examine how chemical bonds and functional groups evolved after each thermal treatment stage, and the results are plotted in Figure 3a. It can be observed that the melt-spinning process did not have any significant influence on the chemical structure of the as-received S1 asphaltenes as the precursor. Also, the intensity of the aliphatic C–H bending and stretching peaks were reduced after stabilization. This indicates that a significant fraction of the C–H bonds are broken during the stabilization process. Moreover, oxidation leads to the appearance of a slight peak in the range of 1700 cm^{-1} and 1718 cm^{-1}, which correspond to C=O bonds. It has been reported that the disappearance of aliphatic C–H stretching and bending and an increase in C=O content indicate appropriate conditions for oxidation [3]. This is evident through the decrease in H/C and increase in O/C molar ratios shown in Table 1. The two vibrations at 1525 cm^{-1} and 1553 cm^{-1} are assigned to the asymmetrical valence vibration of NO_2 groups bonded to an aromatic or an aliphatic system [4]. Peaks around 1600 cm^{-1} correspond to the aromatic stretching of the C−H ring, and the broad peaks from 920 to 850 cm^{-1} correspond to an out-of-plane aromatic structure. The signal at 1030 cm^{-1} was tentatively assigned to the sulfoxide functional group (S = O) [4]. FTIR analysis did not show absorption peaks for carbonized fibers. This behavior has also been observed in literature for PAN-based carbon fibers [5].

X-ray diffraction (XRD) was used to obtain information on the degree of crystallinity of asphaltene-derived fibers, as shown in Figure 3b. As-spun fibers exhibit a broad peak at around 20°, signifying the spacing between alkyl chains or saturated rings. The XRD patterns show a distinct diffraction peak at around 2θ=25° in carbonized fibers, corresponding to the crystal plane (002) graphite structure. Increasing carbonization temperature led to an improvement in the ordering and development of graphite crystallites. Moreover, a peak at around 2θ =43° that corresponds to the (100) plane of graphite layers is present after carbonizing fibers at 1000 °C, indicating an ordered structure and the presence of graphitic layers within the fibers [6].

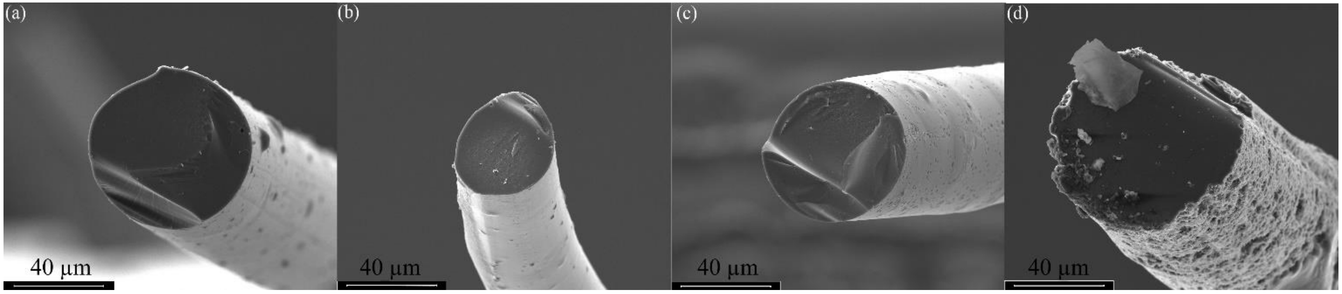

Figure 2. SEM images of (a) As-spun fibers, (b) CF-500 fibers, (c) CF-800 fibers, (d) CF-1000 fibers.

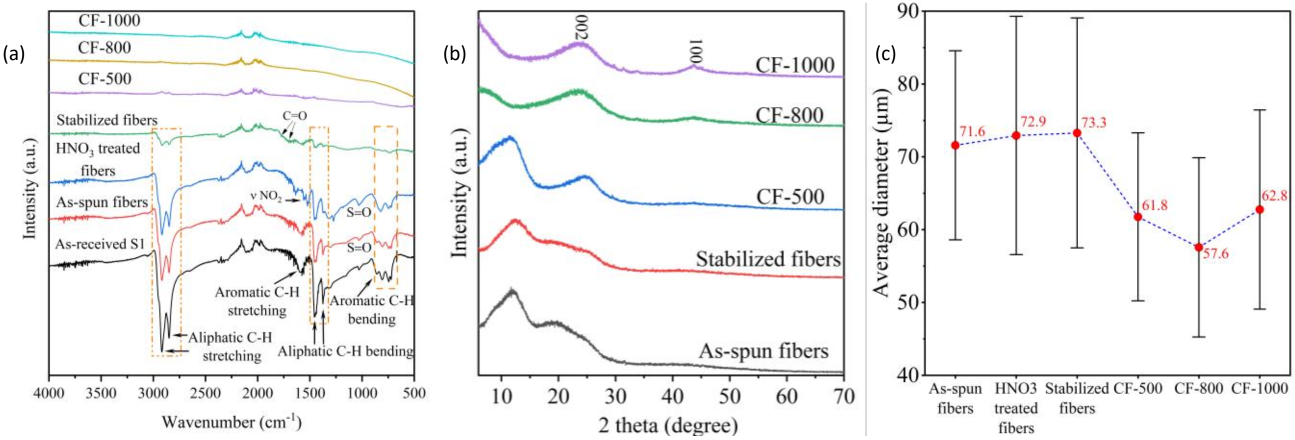

Figure 3. (a) FT-IR spectra, (b) X-ray powder diffraction patterns of S1 asphaltene-derived fibers, and (C) Fiber diameter measurements.

Table 1 indicates the results of the Elemental Analysis used to analyze the CHNS compositions of asphaltene-derived fibers after stabilization and carbonization treatments. The carbon content of the as-spun fibers increased from 80.58% to 88.46% after being carbonized at a temperature of 1000°C. Simultaneously, the H/C ratio reduced from 0.1050 to 0.0016, indicating the occurrence of dehydrogenative condensation. Significantly, even after the carbonization process, the sulfur concentration remains at 8.70 wt%, dispelling our initial hypothesis that they can be the primary source for inducing porosities. Exposure to HNO_3 resulted in nitration by adding NO_2 groups to the aliphatic and aromatic groups, as observed by the increase in nitrogen content [7]. After stabilization, oxygen content reached 8.97 wt%, indicating oxygen diffusion (oxygen uptake) during stabilization. A noticeable reduction in fiber diameter was observed between stabilization and carbonization (Figure 3c), which implies volumetric shrinkage may be responsible for forming large defects in the carbonized fibers. When considered together, the SEM, TGA, and EA data refute the idea that defects observed in carbonized fibers are the result of the volatilization of heteroatoms and low-temperature volatiles. Instead, poor stabilization of the fibers may have resulted in the material not being sufficiently cross-linked to withstand the carbonization process. It has been reported that over 20 wt% of oxygen content after stabilization is an indicator of sufficient oxygen diffusion and reaction during stabilization [7]. The experiments reported a maximum oxygen content of only 9%. Therefore, improving the stabilization process may result in carbon fibers with fewer defects.

Table 1. Elemental analysis of S1 asphaltene-derived fibers

Sample	**H/C**	**O/C**	**C (wt%)**	**H (wt%)**	**N (wt%)**	**S (wt%)**	**O (wt%)**
As-received S1	0.1050	0.0357	80.73	8.47	0.52	7.39	2.89
As-spun fibers	0.1050	0.0358	80.58	8.46	0.90	7.17	2.89
HNO_3 treated fibers	0.1063	0.0462	79.35	8.44	1.24	7.30	3.67
Stabilized fibers	0.0859	0.1172	76.53	6.58	0.98	6.94	8.97
CF-500	0.0406	0.0793	80.63	3.28	1.79	7.90	6.40
CF-800	0.0113	0.0323	86.92	0.99	1.81	7.47	2.81
CF-1000	0.0016	0.0198	88.46	0.15	0.93	8.70	1.76

4 Conclusions

This study involved the fabrication of CFs from as-received S1 AOAs via melt-spinning, followed by chemical (nitric acid) and thermal stabilization and carbonization at various temperatures. Physicochemical characterization was performed on the as-received asphaltenes and produced carbon fibers. Remarkably, the results revealed that the asphaltene-based fibers exhibited significant porosity in the form of surface defects after carbonization at 1000 °C. Although a notable amount of sulfur (~7 wt%) is present in as-spun fibers, these heteroatoms remained in the material, and it does not seem that observed porosity is related to the volatilization of sulfur during carbonization. Microscopic imaging of asphaltene-derived fibers that were carbonized at 500 °C showed no porosity, suggesting that the decomposition of volatile compounds is not the source of porosity as most of them should volatilize before 500 °C based on the TGA results. Significant volumetric shrinkage was observed between the stabilized and carbonized fibers. Further research will include measuring carbonized fibers' specific surface area, pore size, and volume to determine their suitability for potential applications.

5 REFERENCES

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