CLEAN RESOURCES FINAL REPORT PACKAGE

Project proponents are required to submit a Final Report Package, consisting of a Final Public Report and a Final Financial Report. These reports are to be provided under separate cover at the conclusion of projects for review and approval by Alberta Innovates (AI) Clean Resources Division. Proponents will use the two templates that follow to report key results and outcomes achieved during the project and financial details. The information requested in the templates should be considered the minimum necessary to meet AI reporting requirements; proponents are highly encouraged to include other information that may provide additional value, including more detailed appendices. Proponents must work with the AI Project Advisor during preparation of the Final Report Package to ensure submissions are of the highest possible quality and thus reduce the time and effort necessary to address issues that may emerge through the review and approval process.

Final Public Report

The Final Public Report shall outline what the project achieved and provide conclusions and recommendations for further research inquiry or technology development, together with an overview of the performance of the project in terms of process, output, outcomes and impact measures. The report must delineate all project knowledge and/or technology developed and must be in sufficient detail to permit readers to use or adapt the results for research and analysis purposes and to understand how conclusions were arrived at. It is incumbent upon the proponent to ensure that the Final Public Report **is free of any confidential information or intellectual property requiring protection**. The Final Public Report will be released by Alberta Innovates after the confidentiality period has expired as described in the Investment Agreement.

Final Financial Report

The Final Financial Report shall provide complete and accurate accounting of all project expenditures and contributions over the life of the project pertaining to Alberta Innovates, the proponent, and any project partners. The Final Financial Report will not be publicly released.

Alberta Innovates is governed by FOIP. This means Alberta Innovates can be compelled to disclose the information received under this Application, or other information delivered to Alberta Innovates in relation to a Project, when an access request is made by anyone in the general public.

In the event an access request is received by Alberta Innovates, exceptions to disclosure within FOIP may apply. If an exception to disclosure applies, certain information may be withheld from disclosure. Applicants are encouraged to familiarize themselves with FOIP. Information regarding FOIP can be found at http://www.servicealberta.ca/foip/. Should you have any questions about the collection of this information, you may contact the Manager, Grants Administration Services at 780-450-5551.

DEVELOPMENT OF ALBERTA OILSANDS ASPHALTENE (AOA)-BASED CARBON FIBRES

Public Final Report

Prepared for

Alberta Innovates

Prepared by

The University of British Columbia

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Frank Ko, Professor

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Development of Alberta Oilsands Asphaltene (AOA)-based Carbon Fibres**
Alberta Innovates Project Number:	G2020000350
Submission Date:	February 1, 2021
Total Project Cost:	$110,000
Alberta Innovates Funding:	$49,890
AI Project Advisor:	Paolo Bomben

2. APPLICANT INFORMATION:

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Title:	Professor
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3. PROJECT PARTNERS

Please provide an acknowledgement statement for project partners, if appropriate.

RESPOND BELOW

Not applicable.

A. EXECUTIVE SUMMARY

Provide a high-level description of the project, including the objective, key results, learnings, outcomes and benefits.

RESPOND BELOW

The study conducted by Alberta Innovates (AI) through the Bitumen Beyond Combustion (BBC) program concluded that carbon fibre (CF) is the most promising pathway to connect bitumen-derived asphaltene, specifically Alberta oilsands asphaltenes (AOA), to value-added products. However, developing the appropriate cost-effective precursor and processing technologies for CF manufacturing is a major challenge for academic and industry researchers.

Following the BBC program, the Carbon Fibre Grand Challenge (CFGC) is a three-phase program to accelerate the development of large-scale CF production from bitumen-derived asphaltenes. By turning asphaltene into non-combustion and high-value CF products, it can not only reduce the greenhouse emission related to bitumen, but also benefit the related industries. The objective of the CFGC Phase I program is to develop advanced material processing concepts and to address key knowledge gaps for CF fabrication from AOA.

Specifically, our technical approach in this project is to expand the length scale of the fibre diameter to the sub-micron level (nanofibres (NFs)) by the electrospinning (ES) process. To address the fibre spinnability issues, the concept of polymer blending was successfully demonstrated for the ES and melt-spinning (MS) of AOA. The electro-spun polyacrylonitrile (PAN)/AOA NFs can be thermostabilized and consequently converted to carbon fibrous structures including yarns and fabrics. The average diameter of the carbonized NFs (CNFs) was found to be less than 500 nm. It was noted that carbonized mats are flexible and capable of being handled. The chemical structure, thermal properties, and rheological properties of AOA have also been investigated. In addition, polyethylene (PE)/AOA and thermoplastic polyurethane (TPU)/AOA blended melt-spun fibres have been prepared. Rheology studies indicated that the maximum thermal mobility of AOA is around 225 °C, which can be the processing window for AOA. Melt-spun pristine AOA fibres were found to be brittle. Thus, pretreatment, polymer blending, and the addition of plasticizers are required in order to prepare suitable precursors for CF production.

By creating AOA fibres in different forms (fibre architecture)/length scales, this project is expected to result in the development of new technologies, processes, and products that will enable the expansion of the current CF market and the creation of new market opportunities (eg., the electric vehicle market). This is also expected to attract new corporate investment in Alberta and Canada and result in the creation of new ventures that will directly increase jobs and revenue from technology and product exports. In addition, upon the successful development of structural grade, low-cost AOA CFs for automobiles, we will significantly reduce the cost of manufacturing of lightweight structures. Consequently, by enabling the reduction of the structural weight of automobiles, this program will also play an important role in every climate change mitigation strategy globally, including Canada’s, by reducing greenhouse gases (GHG) through structural weight reduction.

B. INTRODUCTION

Please provide a narrative introducing the project using the following sub-headings.

- **Sector introduction:** Include a high-level discussion of the sector or area that the project contributes to and provide any relevant background information or context for the project.
- **Knowledge or Technology Gaps:** Explain the knowledge or technology gap that is being addressed along with the context and scope of the technical problem.

RESPOND BELOW

The global CF market was valued at US$4.7 billion (B) in 2019 and is expected to grow at a compound annual growth rate (CAGR) of 11-12% to reach US$7.8B, and US$13.3B, by 2025, and 2029, respectively. The anticipated growth of the CF market is largely due to the increasing demand for fuel-efficient and lightweight vehicles in the automobile industry. For instance, in the automotive industry, CF composites are only introduced in high-end and luxury cars due to their high cost (US$17-33/kg) with 50% of the cost attributed to the cost of the precursor polymers, such as polyacrylonitrile (PAN). If this cost decreases to US$11-15/kg, CF will be used on a much larger scale. With the availability of low-cost CF (LCCF), there will be increased use of CF in the automotive industry, rather than limited to luxury cars and the aerospace industry, where high-grade CF is used. There are also many new applications of CF-based composite which are not yet commercially feasible as they are expensive. Therefore, developing low-cost precursors and processing technologies for CF manufacturing is a major challenge for researchers and key manufacturers[1–3]

CFs are lightweight and have excellent strength, low specific gravity, outstanding modulus of elasticity, high corrosion resistance, and high moldability. Continuous CFs offer higher tensile strength when compared to other types of CF products. These fibres can be used in layup, weaving, prepregging, filament winding, braiding, and pultrusion processes for manufacturing composites parts for various end-use industries. It must be noted that CF is a long, thin strand of material made from carbon, where its carbon content is more than 90% for standard modulus carbon and almost 100% for high modulus CF. CF produced from precursors, such as PAN, pitch, rayon, or other organic fibres in an inert atmosphere to dissociate elements other than carbon[4–6].

Asphaltene (containing 50-60% aromatic carbons) could be a great source for many applications, such as paving materials on roads, shingles for roofs, waterproof coatings on building foundations, and CF. Among the large number of potential asphaltene-based products, CF has been identified as one of the highest value-adding options. The inherent superior specific mechanical, electrical, and thermal properties of CF enable their applications in a broad range of products. Considering the high price and limited availability of PAN, the production of LCCF is one of the most promising valorization routes for Asphaltene, which is both economically and environmentally attractive[7–9].

The level of interest in Asphaltene-based carbon fibre (ABCF) is evident in some recent government and industry programs; for example, Honeywell Federal Manufacturing & Technologies under the US Department of Energy (DOE) contract filed two US patents[10,11]. Even though both patents and their previous versions provide processing information, there is a very limited record of the fibre diameter and its mechanical properties. The merely reported data is: "In one or more embodiments, the composites will have a tensile strength of at least about 300 MPa.". It shall be noted that "Carbon fibres for use in the invention include those derived from PAN, pitch, asphalt, phenolic fibres, rayon, cotton, lignin, or any other Suitable natural product, or any other suitable carbon fibre precursor."[10,11]. Zuo et al. reported the mechanical properties of the coal-derived ABCF, and the tensile strength and elastic modulus were 1.0 GPa and 350 MPa, respectively[12]. Prior to this work, the functionality of pitch-based CF had been studied[13,14]. Ni et al. produced ABCF after chemical modification of Asphaltene with styrene-ethylene-butylene-styrene (SEBS). It is claimed that the average diameter of the CF was 14 µm, and the average tensile strength was over 800 MPa[15]. The tensile strength was higher than that of reported CF from coal tar pitch (414 MPa and 662.3 MPa)[16,17]. In a later publication, this group reported that their ABCF reached a tensile strength of 0.92 GPa[18]. Following the work, they studied the application of these fibres as supercapacitor electrode material with high specific capacitance[19].

Despite these research activities, it is recognized that from the current state of the art, these materials do not lend themselves to primary structural applications. Compared to conventional CFs created from PAN, their strength properties are significantly lower. Specifically, to be qualified for automotive composites, the strength and modulus requirements are 1.72 GPa and 172 GPa, respectively[20]. Thus, several knowledge gaps need to be addressed to have AOA CF with desirable properties. The scientific fundamentals, including the chemical and physical properties of the AOA feedstock for CF production, are still largely unknown and need to be characterized. Moreover, the impacts of impurities, such as sulfurs and metals in AOA on the CF production process still need to be investigated. In addition, the requirement of mesophase formation for AOA CF is still uncertain.

It is believed that making fibres of smaller diameter would help reduce the defects and promote quantum efficiency, surface energy and reactivity, thermal and electrical conductivity. Thus, nanofibres (NFs) have the potential to not only address the manufacturing challenges but also provide new opportunities for product development. Besides, the polymer blending technique has been applied to produce suitable precursors for CF. By introducing proper blend ratios with good miscibility, it could enhance the spin-ability, flexibility, as well as physical and chemical properties of the resulting fibres[21–23]. Accordingly, we hypothesize that by combining the advantages of NFs and the polymer blend, a new class of low-cost hybrid CF and fibrous assemblies can be developed for structural applications, such as automobile composites and functional applications, such as electromagnetic shields and fuel cell electrodes.

C. PROJECT DESCRIPTION

Please provide a narrative describing the project using the following sub-headings.

- **Knowledge or Technology Description:** Include a discussion of the project objectives.
- **Updates to Project Objectives:** Describe any changes that have occurred compared to the original objectives of the project.
- **Performance Metrics:** Discuss the project specific metrics that will be used to measure the success of the project.

RESPOND BELOW

Knowledge or Technology Description: Developing the appropriate cost-effective precursor and processing technologies for carbon fibre (CF) manufacturing is a major challenge for researchers and key manufacturers. It is believed that making smaller fibres would help reduce the defects and promote quantum efficiency, surface energy and reactivity, thermal and electrical conductivity. Thus, nanofibres (NFs) have decent potential to not only address the manufacturing challenges but also provide new opportunities for product development. Moreover, by applying the polymer blending technique, it can further improve the properties of the resulting fibre. In this project, the main objective is to produce NFs from Alberta Oilsands Asphaltenes (AOA) by electrospinning (ES), thermostabilization, and carbonization of the NFs. The chemical, thermal, and rheological properties of AOA feedstock were characterized. Melt-spinning (MS) of AOA with suitable polymer blends was also investigated.

Updates to Project Objectives: There are no changes to the original objectives of the project.

Performance Metrics: The produced AOA-based CF will be studied and characterized based on physical appearances, such as flexibility and capability of being handled, morphology, fibre diameter, and mechanical and electrical properties.

D. METHODOLOGY

Please provide a narrative describing the methodology and facilities that were used to execute and complete the project. Use subheadings as appropriate.

RESPOND BELOW

1. Electrospinning (ES)

To assess the feasibility of improving the strength and modulus for Asphaltene-based carbon fibre (ABCF), our approach focused on a combination of material concept and fibre-forming process.

Material concept: Pitch (including asphaltene)-based precursors have a lower cost compared to PAN-based precursors. They show a better elastic modulus, but an extremely low failure strain and inferior tensile strength compared to PAN-based carbon fibres. Thus, the development of a new class of CF precursors, which is a blend of PAN with pitch precursors, can enhance fibre spinning resulting in a combination of better ductility, lower cost, and greater modulus and strength. Manufacture of hybrid precursors can reduce cost and improve mechanical properties including reducing the likelihood of brittleness observed in pitch fibres.

Fibre-forming process: It is well known that molecular order (crystallinity) and molecular orientation play a critical role in the strength and toughness of fibres. In addition, it has been well established that the strength of fibres increases as fibre diameter decreases. Although there are several alternative methods for generating fibres in a submicron level, none matches the popularity of ES technology. ES is a simple and scalable method to produce submicron fibre[24–28].

In this research, the ES process is selected for the fabrication of AOA-based NFs. ES uses electrostatic force to generate ultra-fine fibres. Figure 1 shows a typical ES set-up: a polymer solution is placed in a syringe with a metal tip that is charged with high voltage, and an electric field is generated between the metallic collector and the needle tip. A uniform jet of polymer forms when the voltage reaches a critical value and overcomes the surface tension of the deformed droplet (the Taylor Cone) of the polymer solution. The jet diameter can be modified via electrically induced bending instability, which results in hyperstretching and rapid evaporation of the solvent. Random (non-woven) fibrous mats can accumulate on the collector surface, or aligned fibrous mats can be produced through proper control of the electrodes and the use of rotating drums. Many processing parameters can influence the spinnability and physical properties of electrospun NFs. In spinning AOA-based CNFs, the main objective is to reduce the fibre diameter to increase the tensile strength. The diameter of NFs can be controlled by adjusting certain process parameters, such as surface tension, the dielectric constant of the spinning dope, flow rate, current carried by the fibre, and the ratio of the initial jet length to the nozzle diameter[25]. Fibres obtained from AOA polymer blends were thermostabilized, carbonized, and consequently characterized.

Characterization: Scanning electron microscopy (SEM), optical microscopy, Fourier-transform infrared (FT-IR) spectroscopy, mechanical properties, and electric conductivity.

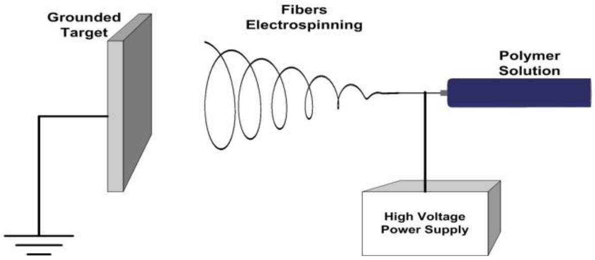


Fig.1. Schematic of the Electrospinning Process.

2. Meltspinning (MS)

In addition to electrospinning (a solution spinning pathway), we also investigated the feasibility of AOA polymer blends for meltspinning (MS). With suitable polymer blends, the resulting fibres could have good compatibility with AOA to increase the spinnability and flexibility of melt-spun fibres.

Materials: Alberta oilsands asphaltene (AOA) was obtained from Alberta Innovates. Polyethylene (PE) was obtained from Sigma-Aldrich. Thermoplastic polyurethane (TPU) was obtained from Covestro.

Fiber Preparation: Samples were extruded using a Dynisco LME extruder system and the Xplore MC15 micro compounder. For MC 15 micro compounder, the screw speed was 100 rpm for compounding and 25 rpm for fiber spinning.

Characterization: Fourier transform infrared spectroscopy (FT-IR) measurement was conducted using a Bruker INVENIO spectrometer over the range 400–4000 cm^{-1} equipped with an attenuated total reflectance accessory (ATR), a total of 32 scans with a spectral resolution of 2 cm^{-1} were recorded.

The Thermalgravimetric analysis (TGA) was conducted using the Q500 analyzer from TA Instruments. The sample was heated from 20 °C to 800 ° C at a heating rate of 10 °C/min with an N_2 flow.

The rheological analysis was performed utilizing an Advanced Rheometer (AR 2000) equipped with an environmental test chamber from TA Instruments. The samples were measured using a temperature ramp mode of 3 °C/min from room temperature to 300 °C between aluminum parallel plates at an angular frequency of 1 rad/s.

E. PROJECT RESULTS

Please provide a narrative describing the key results using the project's milestones as sub-headings.

- Describe the importance of the key results.
- Include a discussion of the project specific metrics and variances between expected and actual performance.

1. Electrospinning (ES)

In the first stage of this work, we studied the fibre formation of: (1) pristine AOA; (2) AOA blended with PEO (polyethylene oxide); and (3) AOA blended with PAN (polyacrylonitrile). Figure 2 shows the images of 10, 20, and 30 weight percent (wt.%) of AOA solutions with/without 1 and 5 wt.% PEO. Our experiment with AOA revealed that pristine AOA solutions cannot form fibrous structures (Fig.2 a-c). In the next series of experiments, we studied the effect of PEO on the fibre formation. It was found that by blending 1wt.% PEO, fibrous structures can be fabricated. However, these fibres were not uniform and beads-free (Fig.2 d-l). In addition, it was observed that by increasing the AOA concentration, the fibre diameters increased. Among the samples containing 1wt.% PEO, the fibre morphology of the 20wt.% AOA (Fig.2 g-i) demonstrated a better fibre formation than the others. In the next stage, we tried to answer the question "Would increasing the PEO concentration improve the fibre formation?" The results showed (Fig.2 m-u) that adding 5wt.% PEO did not have a significant effect on the fibre formation. It should be noted that adding 5wt.% PEO to 30 wt.% AOA solution resulted in gelation and could not form fibre (Fig. 2u). Therefore, PEO is not a suitable blending polymer for AOA at the ratios tested.

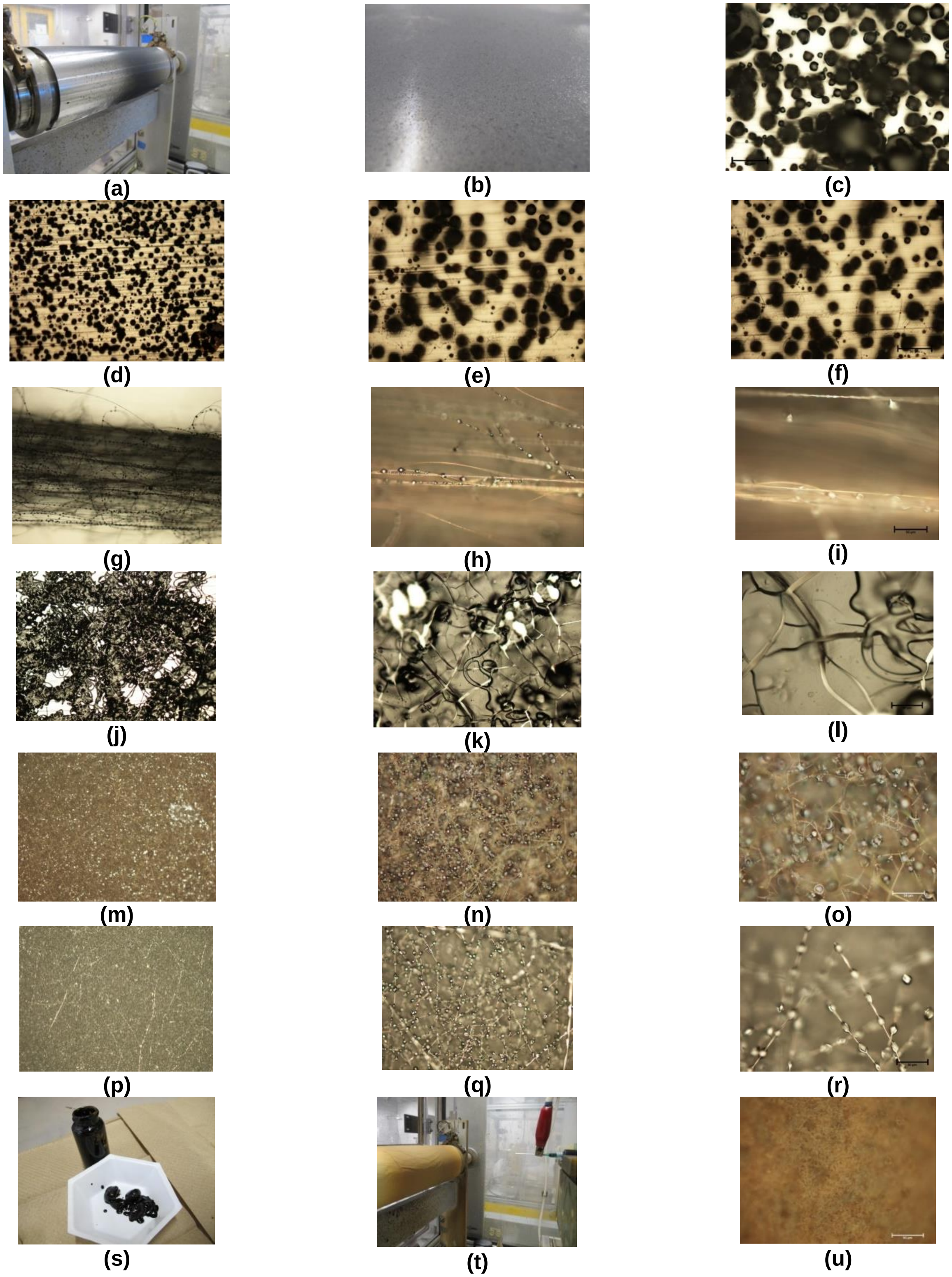


Fig. 2 (a(x1), b(x1), c(x50)) Pristine AOA; (d(x5), e(x20), f(x50)) 10wt.%AOA/PEO(1%); (g(x5), h(x20), i(x50)) 20wt.%AOA/PEO(1%); (j(x5), k(x20), l(x50)) 30wt.%AOA/PEO(1%); (m(x5), n(x20), o(x50)) 10wt.%AOA/PEO(5%); (p(x5), q(x20), r(x50)) 20wt.%AOA/PEO(5%); (s(x1), t(x1), u(x50)) 30wt.%AOA/PEO(5%).

In the next series of experiments, we studied the effect of the blending ratio of AOA with PAN on fibre formation. Figure 3 shows the images of different percentages of AOA/PAN polymer blends. The results revealed that the fibrous structures could be fabricated by blending AOA and PAN up to 40/60 ratios (Fig.3 a-i). It was learned that the AOA/PAN (40/60) mix was the maximum ratio suitable for moving forward without any pretreatments. Although it was found that the AOA/PAN (50/50) percent polymer blend could not result in a fibrous structure (Fig.3k), there is a possibility that AOA pretreatment may produce fibrous structures. In addition, it must be noted that the existence of the particles in the fibres (Fig.3f), which may be the result of the impurities in the AOA. This shall be studied in greater detail in Phase II of the carbon fibre program. Our approach to addressing this issue is to fractionate AOA by using solvents such as tetrahydrofuran (THF) to separate the impurities/insoluble and then recover the fractionated AOA that can be dissolved and electrospun into NFs.

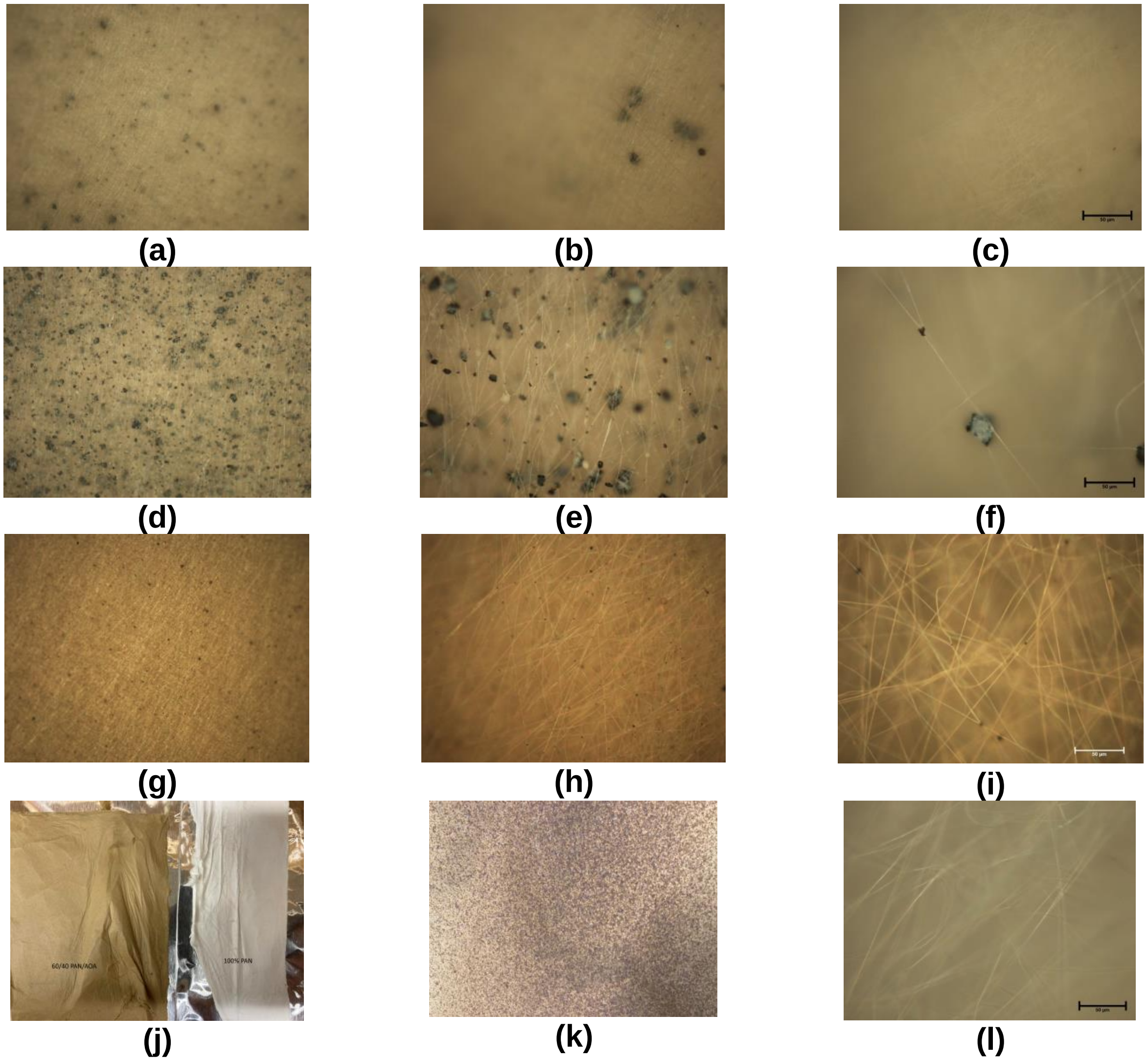
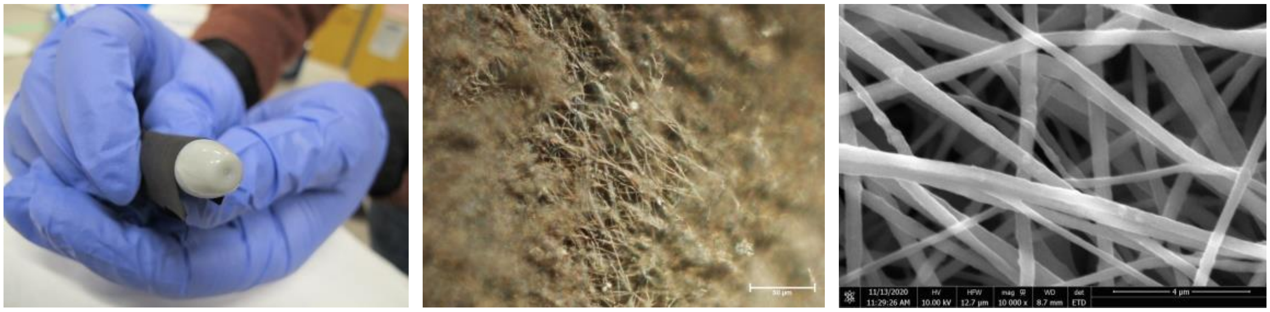


Fig. 3 (a(x5), b(x20), c(x50)) Solution Mix AOA/PAN:10/90; (d(x5), e(x20), f(x50)) Solution Mix AOA/PAN:20/80; (g(x5), h(x20), i(x50)) Solution Mix AOA/PAN:40/60; j(x1) E-spun nanofibre mats; k(x1) Solution Mix AOA/PAN:50/50; l(x50) 100% PAN nanofibres.

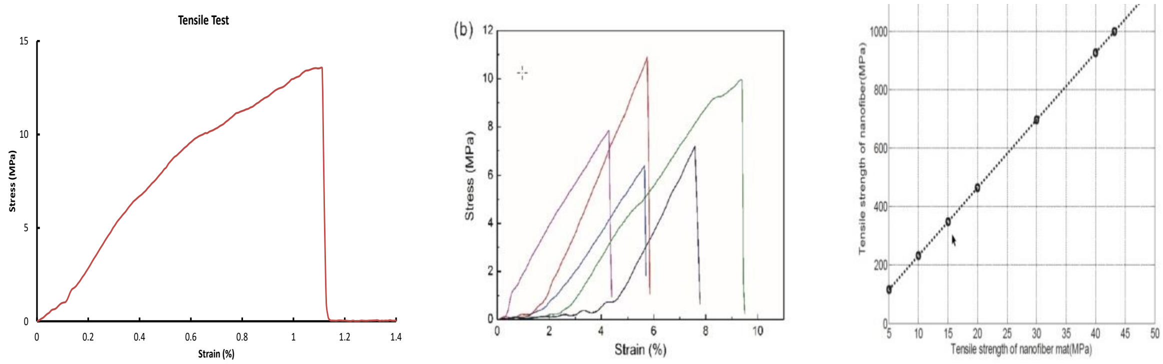
In the next stage of this work, we studied the feasibility of carbonization of the highest polymer blend ratio (AOA/PAN: 40/60). Figure 4 shows the images of the carbonized NF mats. It was noted that carbonized mats bend over the radius of curvature of 0.75 cm without failure, manifesting flexibility and handleability (Fig.4a). SEM images (Fig.4c) revealed that CF diameters reduced up to 0.5 micron, which to the best of our knowledge, no research group has reported less than 2 microns, up-to-date. It is believed that this material is suitable for electrodes used in batteries and/or supercapacitors. To confirm this hypothesis, we studied the mechanical and electrical properties of these CF mats.



(a) (b) (c)

Fig. 4 a(x1) image of CF mat; b(x50) OM image of CF; c(x50) SEM image of CF.

Tensile Test: Figure 5a shows a typical stress-strain curve of the PAN/AOA electro-spun CF mats, which is comparable with published results for the PAN electro-spun CF mats (Fig.5b)[25]. Using a fibre web model developed in our labs (Fig.5c) we can relate the tensile strength of fibre mats to individual nanofibres and tailor the mechanical properties of the fibres.



(a) (b) (c)

Fig. 5 (a) Stress-strain curves of PAN/AOA CF mats; (b) Stress-strain curves of PAN CF mats; (c) Predicted tensile strength of individual nanofibre vs. the tensile strength of nanofibre mats

Electrical Properties: According to collected data for the sheet resistance of the PAN/AOA (Fig.6), the electrical conductivity of the PAN/AOA electro-spun CF mats is comparable to published results for PAN electro-spun CF mats[29]. It must be noted that we can tailor the performance of the mat, based on our previous studies[25,30,29].

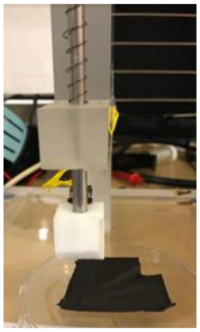


Fig. 6 Sheet resistance measuring device.

2. Melt-spinning (MS)

FT-IR spectroscopy was applied to characterize the chemical structures of asphaltene powders. As shown in Figure 7, the peaks at 746, 809, and 857 cm^{-1} are attributed to aromatic C-H bending, and the peak at 1595 cm^{-1} can be assigned to the aromatic C=C stretching. The peaks at 1373 and 1447 cm^{-1} are assigned to aliphatic C-H bending, and the bands at 2850 and 2918 cm^{-1} are corresponding to aliphatic C-H stretching. The FT-IR result indicated similar peak assignments and characteristic structures with previous research[15,26].

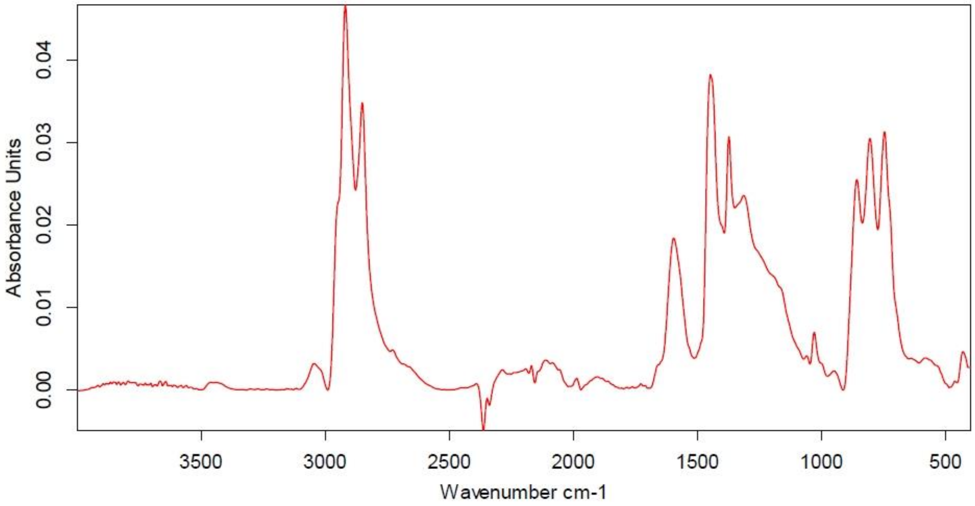


Figure 7. FT-IR spectra of AOA

The thermal stability of AOA was studied by Thermalgravimetric analysis (TGA), as shown in Figure 8. The thermal behavior of asphaltene was examined under N_2 flow from ambient temperature to 800 °C at the 10 °C/min heating rate. The result demonstrated that AOA exhibited thermal degradation (5% weight loss) at 392 °C, followed by a significant weight loss between 400 °C and 550 °C. The maximum weight loss was observed at 495 °C, as indicated by the sharp peak in the differential thermal analysis (DTA) curve. And the residue after the heat treatment was 66.80 %

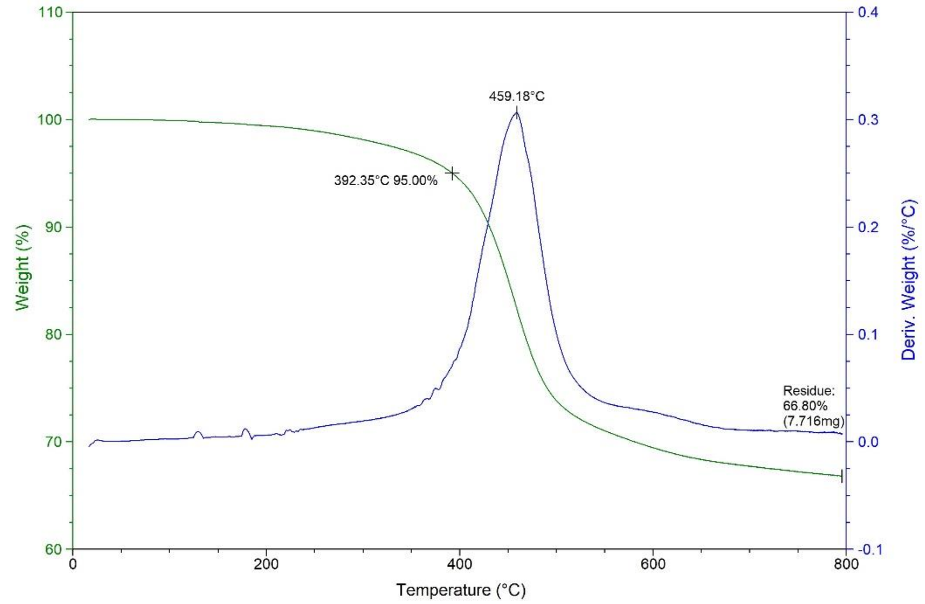


Figure 8. TGA curves of AOA

The rheological analysis was conducted to determine the viscoelastic behavior of the AOA. Asphaltenes have suitable softening points with good rheological properties is critical for melt spinning[21,31,32]. AOA powder heated from room temperature to 300 °C at 3 °C/min heating rate under nitrogen flow between parallel plates, and Figure 9 shows the complex viscosity as a function of the temperature of AOA powder. The Tan delta peak at 225 °C indicates the maximum thermal mobility of AOA, and it could be related to a thermal transition temperature for AOA. The high thermal mobility of AOA in this temperature range could be the processing window of AOA for melt spinning. The storage modulus (G') increased above 250 °C, and it might be due to the sample densification. The storage modulus of AOA is always greater than the loss modulus (G''), which also indicates that the AOA has more solid-like behavior in this temperature range. The addition of plasticizers could help to reduce the storage modulus of AOA and get more of a liquid-like behavior around 200 °C to increase the spinnability. Pretreatment of asphaltenes, such as thermal condensation by air blowing could also help turn the asphaltene into a spinnable precursor and the mesophase formation for the later thermal treatment process[15,18,19,33].

Carbon materials with crystalline and planar mesophase structures play an important role in the manufacture of carbon fibres with excellent modulus, and carbon electrodes with electric conductivity for energy storage devices[34–36]. The anisotropic structure and rheology behavior of the mesophase carbon also determine the graphitization, mechanical, and spinning properties of carbon fibre[37]. Research has been done by using coal liquid extract asphaltene as the feedstock to produce mesophase carbon[38,39]. It was found that through the heat treatment at an inert atmosphere at 400 °C for 180 min, it could have 79% of mesophase structure with 12.4% yield due to the polymerization and thermal condensation reactions of the hydrocarbons[39]. The aliphatic functional groups in asphaltene could suppress the growth of mesophase[38] and have an adverse impact on mesophase development[36]. Based on the thermal analysis and rheology results for AOA, the suitable processing temperature window of

AOA could be the temperature range around 225 °C, while the AOA still has more solid-like behavior. Rheology analysis with a higher temperature range should be done to know better about the mesophase formation temperature range for AOA. More properties characterization such as Fourier Transform Infrared Spectrometer (FT-IR), nuclear magnetic resonance (NMR), and x-ray diffractometry (XRD) need to be done for a better understanding of the requirement of mesophase formation in AOA.

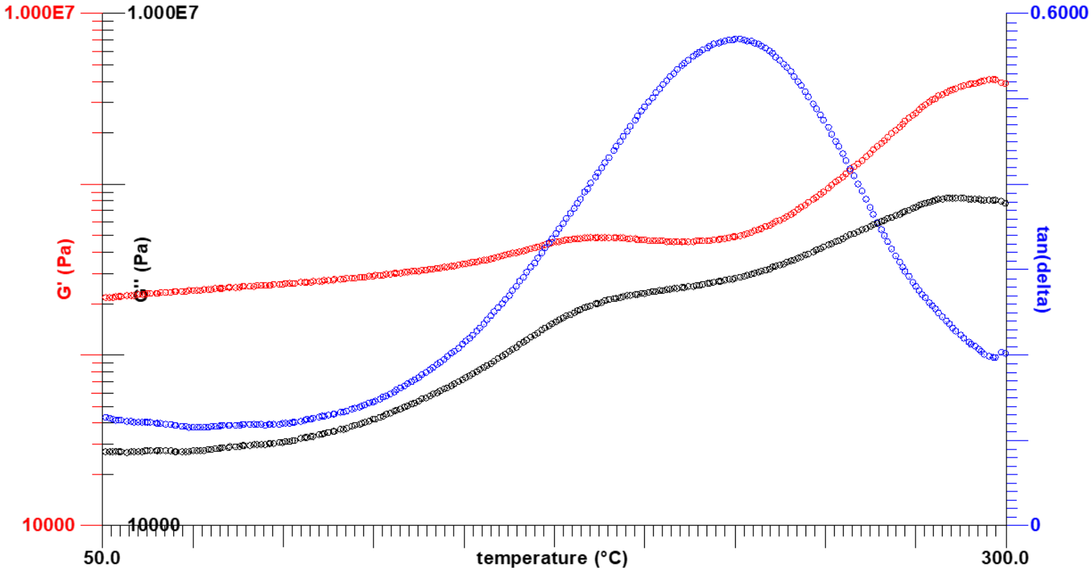


Figure 9. Storage and loss modulus and tan δ as a function of temperature for AOA

After the characterization of thermal properties of AOA, as-received AOA powder was melt-spun into fibre by using Dynisco LME extruder. It was found that AOA can be melt-spun in the range of 180-250 °C, while the molten AOA was highly viscous and the pure AOA as-spun fibres were brittle and hard to form a continuous filament. Moreover, the as-spun short fibres were tended to fuse during the following thermal treatment process even at the low heating rate (0.5 °C/min). It was considered that the pure as-received AOA powder was unsuitable for the fabrication of melt-spun fibres. The pretreatment of AOA powder, the addition of plasticizers, and the polymer blending with AOA are critical to make AOA a suitable precursor for CFs.

Since AOA was difficult to melt-spun into continuous filaments, polyethylene (PE) is considered to blend with AOA to make composite fibres. PE has been utilized as the precursors for CFs manufacturing and is the potential candidate for polymer blending with AOA[40]. Pure PE can be steadily melt-spun starting at 140 °C with the Dynisco extruder system, and the fibre diameter ranged from 100-20 microns. PE/AOA with different ratios were prepared and Figure 10 a-f show the optical microscope (OM) and polarized OM images of the precursor fibres of PE/AOA (70/30) (Figure 10 a, b), PE/AOA (75/25) (Figure 10 c, d), and PE/AOA (80/20) (Figure 10 e, f). It was found that PE/AOA blended melt-spun fibres can be fabricated with a PE ratio greater than 50%, and the fibre diameter ranged from hundreds to ~50 µm. PE/AOA 70/30 could form a continuous filament, while the as-spun fibre was still brittle with non-uniform fibre diameter and had many bumps and aggregations on the surface (Figure 10 (a) and (b)).

The fibre morphology and flexibility increased with the increase of PE/AOA ratio. PE/AOA 80/20 could have flexible fibres with uniform diameter, while the fibres still have a rough surface and phase separations between PE and AOA (Figure 10 (e) and (f)). The incompatible polymer blends could create voids and porous structures during the thermal treatment process[23]. The thermal behavior of PE and AOA needs to be further investigated to improve the polymer blending, and the spinning conditions need to be further optimized to enhance the spinnability.

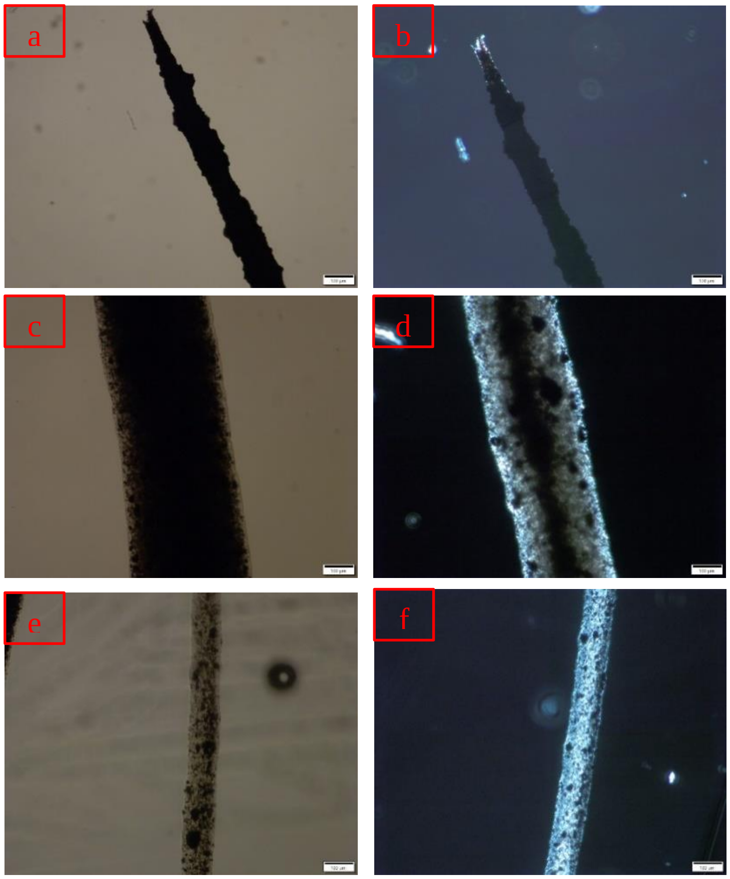


Figure 10. OM and polarized OM images of melt-spun fibres obtained from PE/AOA_70/30 (a, b), 75/25(c, d), and 80/20(e, f)

Besides PE, thermoplastic polyurethane (TPU) has been also applied to blend with polymers for the fabrication of CF precursors. TPU/AOA blend melt-spun fibres can be fabricated with different ratios in the Dynisco extruder, and the fibre diameter range from hundreds to 80 µm. TPU and TPU/AOA 90/10 blending then applied to Xplore MC 15 micro compounder for automatic fibre winding process. Both TPU and TPU/AOA 90/10 can be continuously spun at a winding speed of 70.00 mm/min and winding torque of 150 N-m to produce spools as shown in Figure 11.

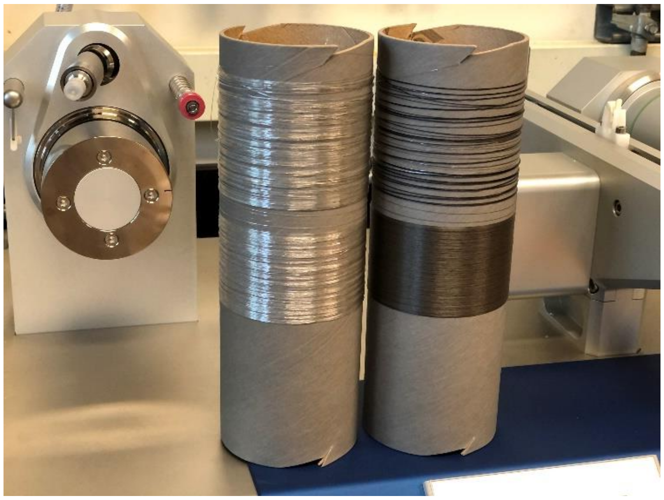


Figure 11. Fibre spools of TPU and TPU/AOA 90/10 (black filaments on the right)

Figure 12 shows the Optical microscope (OM) and polarized OM images of the TPU (Figure 12 a and b) and TPU/AOA (90/10) (Figure 12 c and d) as-spun fibres. The diameter of TPU fibres was ~110 µm, and the diameter of TPU/AOA (90/10) fibres was ~100 µm. The polarized OM images of the TPU/AOA (90/10) demonstrate no phase separation between TPU and AOA, indicating good compatibility of the TPU/AOA blends with some small particles on the edge of fibres. It could be due to the molecular interactions between TPU and AOA polymer chains during the compounding process to create thermodynamically stable polymer blends to prevent phase separation[23]. The fibre diameter can be further reduced by optimizing the fibre spinning process, using smaller dies, and stretching during the fibre winding process[21,23,41].

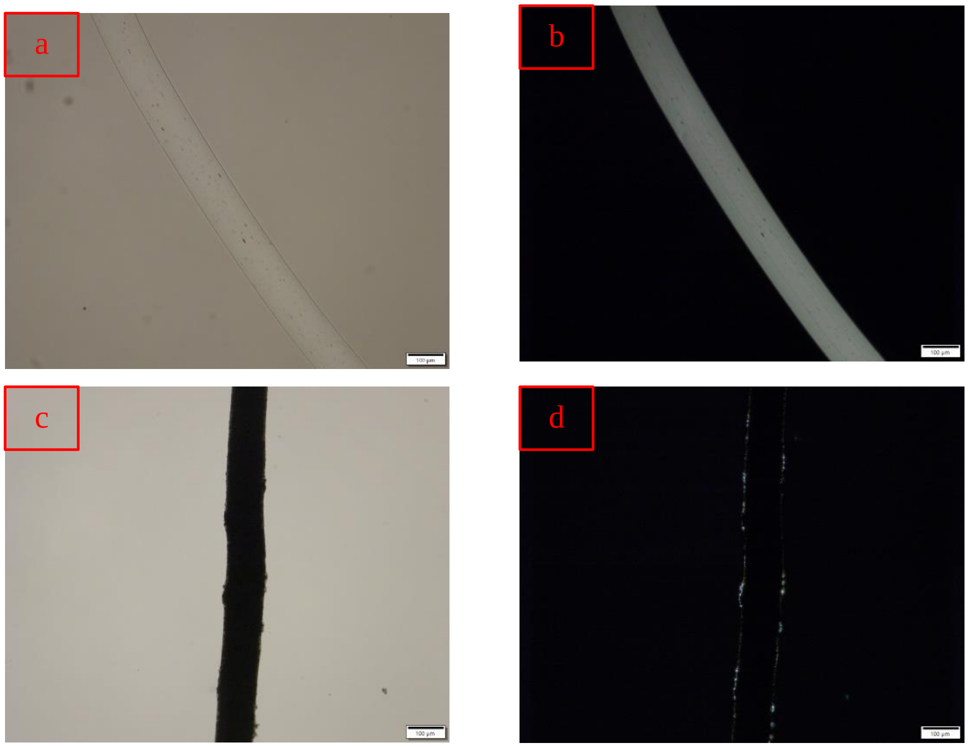


Figure 12. OM and polarized OM images of melt-spun fibres obtained from TPU (a, b) and TPU/AOA 90/10(c, d)

Metrics

Project Success Metrics (Metrics to be identified by Applicant)			
Metric	**Project Target**	**Commercialization / Implementation Target**	**Comments (as needed)**
Tensile Strength	*50-500 Mpa*	*1.75 GPa*	
Modulus	*10-50 Gpa*	*175 Gpa*	

Regarding the project outcomes compared to the project target (table above) for phase I, we met our targets. We are confident that we will meet our targets that cover a range of properties associated with primary and secondary structural applications.

F. KEY LEARNINGS

Please provide a narrative that discusses the key learnings from the project.

- Describe the project learnings and importance of those learnings within the project scope. Use milestones as headings, if appropriate.
- Discuss the broader impacts of the learnings to the industry and beyond; this may include changes to regulations, policies, and approval and permitting processes

RESPOND BELOW

In this study we learned that AOA is not readily fibre forming. However, AOA polymer blends can be transformed into fibrous structures. These structures can be thermostabilized and consequently converted to carbon fibrous structures. The electrospun fibres shrunk during the heat treatment process, thus the diameter of the carbon nanofibers (CNFs) is smaller than the pristine and thermostabilized AOA NFs. The fibre shape is preserved after heat treatment. The average diameter of the AOA CNFs was found to be less than 500 nm, as shown on the SEM images. It was noted that carbonized mats are flexible and handleable.

The chemical structure, thermal properties, and rheological properties of AOA have been investigated; and the PE/AOA and TPU/AOA blended melt-spun fibres have been prepared. Rheology studies indicate maximum thermal mobility of AOA is around 225^{o}C, which can be the processing window for AOA. AOA melt-spun fibres were brittle; thus, pretreatment, polymer blending, and the addition of plasticizer are needed in order to have suitable precursors for CF production. Polymer blending of PE/AOA and TPU/AOA melt-spun fibres were fabricated, and TPU/AOA fibres can be continuously melt-spun to produce spools of flexible filaments with a good blending of these two polymers.

G. OUTCOMES AND IMPACTS

Please provide a narrative outlining the project's outcomes. Please use sub-headings as appropriate.

- **Project Outcomes and Impacts:** Describe how the outcomes of the project have impacted the technology or knowledge gap identified.
- **Clean Energy Metrics:** Describe how the project outcomes impact the Clean Energy Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Program Specific Metrics:** Describe how the project outcomes impact the Program Metrics as described in the *Work Plan, Budget and Metrics* workbook. Discuss any changes or updates to these metrics and the driving forces behind the change. Include any mitigation strategies that might be needed if the changes result in negative impacts.
- **Project Outputs:** List of all obtained patents, published books, journal articles, conference presentations, student theses, etc., based on work conducted during the project. As appropriate, include attachments.

Project Outcomes and Impacts:

The successful implementation of this technology or use of the knowledge generated could result in:

- Improvements of thermal and electrical conductivity, and mechanical properties of AOA-CF.
- Partnerships between End-to-End players in CF industries, from production to consumption.
- Commercial uses of AOA-CF in the automotive industry.

Clean Energy Metrics:

Clean Resources Metrics (Select the appropriate metrics from the drop down list)

Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
$ Future Investment	e.g. $XXX to develop and launch a database to host testing data	15000000	
# of Publications	1	4	
# Students (Msc., PhD, Postdoc)	2	10	
$ in Clean Technology	$49,890		Alberta Innovates' project contribution

Regarding the project outcomes compared to the project target (table above) for phase I, we met our targets (we agreed to hold on the publication due to patent pending). We are confident that we will meet our targets, e.g. reductions in the cost of CF and CO_2 emissions.

Program Specific Metrics:

Program Specific Metrics (Select the appropriate program metrics from the drop down list)			
Metric	Project Target	Commercialization / Implementation Target	Comments (as needed)
# of End Users participating	1	2	commmercial implementation which includes multiple end users in Carbon fibres.
Unique product/process	1	1	
# commercial BBC products	0	1	

The impurities and sulfur content can adversely impact the spinnability and mechanical properties of the resulting fibres. These issues can be addressed by using the fractionation process to purify the feedstock, and by applying electrospinning (ES) to fabricate nanofibres (NFs) to reduce the defects. AOA can be fractionated by using solvent, such as tetrahydrofuran (THF) to separate the impurities/insoluble and then recovered the fractionated asphaltene can be dissolved and electrospun into NFs. Thus, we shall study the basis and chemistry of the impurities, and their impacts on the properties of the fibrous structures. Also, we shall explore an economical approach for reducing/eliminating these impurities.

Project Outputs: We are planning to obtain patents, publish journal articles, attend conference presentations, and have one-to-one meetings with interested potential industrial partners, based on work conducted during the project.

Please provide a narrative outline the project's benefits. Please use the subheadings of Economic, Environmental, Social and Building Innovation Capacity.

- **Economic:** Describe the project's economic benefits such as job creation, sales, improved efficiencies, development of new commercial opportunities or economic sectors, attraction of new investment, and increased exports.
- **Environmental:** Describe the project's contribution to reducing GHG emissions (direct or indirect) and improving environmental systems (atmospheric, terrestrial, aquatic, biotic, etc.) compared to the industry benchmark. Discuss benefits, impacts and/or trade-offs.
- **Social:** Describe the project's social benefits such as augmentation of recreational value, safeguarded investments, strengthened stakeholder involvement, and entrepreneurship opportunities of value for the province.
- **Building Innovation Capacity:** Describe the project's contribution to the training of highly qualified and skilled personnel (HQSP) in Alberta, their retention, and the attraction of HQSP from outside the province. Discuss the research infrastructure used or developed to complete the project.

RESPOND BELOW

H. BENEFITS

The "Benefits" of this approach can be summarized into the following categories:

Economic: This project is expected to result in the development of new technologies, processes, and products that will both attract new corporate investment in Alberta and Canada and result in the creation of new ventures that will directly increase jobs and revenue from technology and product exports. In addition, it is believed that:

- Development of AOA/PAN blends (as a new class of CF precursors) can enhance fibre spinning resulting in a combination of better ductility, lower cost, and greater modulus and strength;
- Manufacturing of this hybrid precursor can reduce costs and improve mechanical properties including reducing the likelihood of brittleness observed in pitch fibres.

Environmental: Upon successful development of structural grade, low-cost AOA carbon fibres for automobiles, we will significantly reduce the cost of manufacturing lightweight structures. Consequently, by enabling the reduction of the structural weight of automobiles, this program will also play an important role in every climate change mitigation strategy globally, including Canada's, by reducing greenhouse gases (GHG) through structural weight reduction.

Social: This project outcome will help transform Canada's AOA resource sectors and accelerate growth in advanced manufacturing, and ensure Canada's maintenance of a strong AOA industry and the associated high-paying jobs. In addition, it is believed that:

- It is well known that molecular order (crystallinity) and molecular orientation play a critical role in the strength and toughness of fibres. It has also been well established that the strength of fibres increases as fibre diameter decreases. Thus, electrospinning (ES) process will improve the mechanical properties of our produced fibres.
- Our ES will be able to scale up easily, since ES is a simple and scalable method to produce submicron fibres.
- In short, we hypothesize that by combining the advantages of nanofibres (NFs), and the AOA/PAN blend, a new class of low-cost hybrid CF and fibrous assemblies can be developed for structural applications, such as automobile composites, civil infrastructures (concrete and wood beam reinforcement, and functional applications, such as electromagnetic shields and fuel cell electrodes.

Building Innovation Capacity: The project has a direct impact on the training of the needed personnel for the new advanced composites and CF industry. It is expected that this program will contribute directly to the education of a new generation of technically capable and environmentally conscious HQPs. The technological advancements contributed by the HQPs will eventually benefit Alberta, the Canadian AOA products industry, and the Canadian economy.

I. RECOMMENDATIONS AND NEXT STEPS

Please provide a narrative outlining the next steps and recommendations for further development of the technology developed or knowledge generated from this project. If appropriate, include a description of potential follow-up projects. Please consider the following in the narrative:

- Describe the long-term plan for commercialization of the technology developed or implementation of the knowledge generated.
- Based on the project learnings, describe the related actions to be undertaken over the next two years to continue advancing the innovation.
- Describe the potential partnerships being developed to advance the development and learnings from this project.

RESPOND BELOW

To realize the opportunities derived from AOA-based CF (AOA-CF), we must overcome several challenges crucial for the performance of the CF, including mechanical and physical properties, and productivity. The next steps/solutions to the various challenges are summarized herein. The main challenges for AOA-CF include the purification of asphaltene precursors and the defects mitigation of fibre during the extrusion process. The impurities and sulfur content can highly impact the spinnability and mechanical properties of the resulting fibres. These issues can be addressed by using the fractionation process to purify the feedstock, and by applying electrospinning (ES) to fabricate nanofibres (NFs) to reduce the defects. AOA can be fractionated by using solvent, such as tetrahydrofuran (THF) to separate the impurities/insoluble and then recovered the fractionated asphaltene can be dissolved and electrospun into NFs. Thus, we shall study the basis and chemistry of the impurities, and their impacts on the properties of the fibrous structures. In addition, we shall explore an economical approach for reducing/eliminating these impurities. AOA can also blend with natural polymers, such as lignocellulosic biomass and/or synthetic polymers, such as polyethylene/polyurethane to make a wide range of polymer blends for CF precursors. These blends can be further reinforced with different nano-fillers, such as carbon nanotubes (CNTs), graphene, and/or nanocrystal cellulose (NCC).

The ES technique can produce a nonwoven structure, which can be an alternative to industries seeking short fibres, that does not involve chopping continuous fibres. The heat treatment process, including thermostabilization and carbonization, also has a significant impact on the CF properties. We shall investigate and characterize the change in chemical and physical properties at each step in the production of AOA-CF, as well as the effects of using different fillers and polymer blends with AOA. While studying the thermal properties of the fibres, we shall also evaluate the formation and stability of mesophase and amorphous domains as a function of composition, chemical structure, and crystallization conditions. At this phase, we used single-needle/nozzle ES. For Phase 2, we will evaluate the feasibility of scaling up the production by using our multi-needle/nozzle ES (MNES) and needle/nozzle-less ES (NLES) units. Both MNES and NLES can provide substantially higher fibre production capacities and utilization of AOA. Furthermore, we will use melt-spun and melt-blown methods to increase productivity and address the scalability for the microfibres production.

We will also conduct cost analysis and process analysis to study the production economics in terms of energy requirements (e.g. processing energy consumption, i.e. lower thermal stabilization temperature), and GHG emissions of the AOA-CF production using the techniques mentioned above.

Please provide a narrative outlining how the knowledge gained from the project was or will be disseminated and the impact it may have on the industry.

RESPOND BELOW

J. KNOWLEDGE DISSEMINATION

The knowledge gained in this project include the characterization of AOA feed stock, fibre formation by electrospinning and meltspinning process, and CF production with diameter ranging from micron to nano scale expand the market space for CF products.

The gained knowledge will be disseminated through traditional means of journal publications, conference presentations, and workshops organized by the project team. In addition, we are planning to obtain patents and have one-to-one meetings with interested potential industrial partners, based on the work conducted during this project.

To facilitate meaningful knowledge transfer, we will form a Canadian Carbon Fibre Consortium (CCFC) in collaboration with the Composite Research Network(CRN) of which Professor Anoush Poursatip is the director. Just like the pilot scale equipment already available at UBC, CCFC will be dedicated to the AOA project. The CCCF will benefit from the network of Academia, Industry, and Government laboratories with raw material suppliers, academic and industrial manufacturers, and end-users. The CCFC will promote and construct a circular economy for the Canadian CF industry through the supply chain integration from the members. With the development of AOA-based CF, we can create numerous value-added products and opportunities for related industries. Moreover, it will also bring environmental benefits by reducing GHG emissions for a more sustainable future.

K. CONCLUSIONS

Please provide a narrative outlining the project conclusions.

- Ensure this summarizes the project objective, key components, results, learnings, outcomes, benefits and next steps.

RESPOND BELOW

We demonstrated that with a proper polymer blend (right combination/formulation of AOA/PAN), we can produce nanofibres by electrospinning. We confirmed that the produced nanofibres can form CF by applying appropriate temperature at the thermostabilization and carbonization steps. It was noted that the carbonized nanofibre mat is flexible and easy to handle, and the CF diameter is <500nm. Thus, submicron AOA-based CF can be fabricated.

The chemical structure, thermal properties, and rheological properties of AOA have been investigated, and the PE/AOA and TPU/AOA blended melt-spun fibres have been prepared. It was found that TPU and AOA were well blended and can be continuously melt-spun to produce spools of flexible filaments. Rheology studies indicate a possible processing window for AOA; while the pretreatment process, polymer blending, and the addition of plasticizers are needed to have suitable precursors for the AOA melt-spun CF production.

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