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.

Manufacturing of Carbon Fibers from Alberta Asphaltene

Public Final Report

Prepared for

Alberta Innovates

Prepared by

School of Materials Science and Engineering, Georgia Institute of Technology,
Atlanta GA, 30332

Jyotsna Ramachandran, Graduate Student
Casey Smith, Graduate Student
Dr. Kishor Gupta, Senior Research Scientist
Dr. Satish Kumar, Professor *(PI)*

CLEAN RESOURCES FINAL PUBLIC REPORT TEMPLATE

1. PROJECT INFORMATION:

Project Title:	**Manufacturing of Carbon Fibers from Alberta Asphaltene**
Alberta Innovates Project Number:	G2020000336
Submission Date:	February 19, 2021
Total Project Cost:	$50,000
Alberta Innovates Funding:	$50,000
AI Project Advisor:	Paolo Bomben

2. APPLICANT INFORMATION:

Applicant (Organization):	**Georgia Institute of Technology**
Address:	School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta GA, 30332
Applicant Representative Name:	Satish Kumar
Title:	Professor
Phone Number:	404.894.7550
Email:	satish.kumar@mse.gatech.edu

3. PROJECT PARTNERS

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

RESPOND BELOW

None

A. EXECUTIVE SUMMARY

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

RESPOND BELOW

Please see the attached report at the end of this document.

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

Please see the attached report at the end of this document.

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

Please see the attached report at the end of this document.

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

Please see the attached report at the end of this document.

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.

RESPOND BELOW

Please see the attached report at the end of this document.

Project Success Metrics (Metrics to be identified by Applicant)			
Metric	**Project Target**	**Commercialization / Implementation Target**	**Comments (as needed)**
Fiber Spinning	*Ability to spin fiber using asphaltene, fiber stabilization and carbonization, and fiber charaterization*		
Tensile Strength	*1500 Mpa*	*3000 Mpa*	
Tensile Modulus	*100 GPa*	*250 Gpa*	
Flowsheet for CF Process	*1*	*1*	*Project flowsheet will differ from commercial flowsheet*

The project was able to spin asphaltene / polyacrylonitrile blends into fibres. The tensile strength achieved was 1.1 GPa, just below the 1.5 GPa targeted. The modulus of 181 GPa exceeded the targeted 100 GPa. Process parameters for generating carbon fibre using asphaltenes were preliminarily determined in this project. The project demonstrates the preliminary potential for carbon fibre development involving asphaltenes.

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

Please see the attached report at the end of this document.

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 Resources 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.

RESPOND BELOW

- **Project Outcomes and Impacts:** The successful formation of asphaltene / PAN fibers helps to close the gap in understanding of how to blend asphaltenes with polyacrylonitrile to form fibers. More work needs to be done to fully close the gap. The progress made is an important first step forward in combining both feedstocks together as a path for producing lower cost carbon fibre. For a detailed assessment of the technical progress, please see attached report at the end of this document.

- **Clean Resources Metrics:**

Clean Resources Metrics (Select the appropriate metrics from the drop down list)			
Metric	**Project Target**	**Commercialization / Implementation Target**	**Comments (as needed)**
# of Publications	1		Anticipating one publication in phase I of the project.
# Students (Msc., PhD, Postdoc)	1		One graduate students in phase I
$ in Clean Technology	$50,000		
# New products/services created	0	1	

The Clean Resources metrics described in the contract have been met or will be met, with two students participating in the project and at least one publication expected. Additional work would progress the results of this project towards a new product being created.

- **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)**
Unique product/process	1 - Fiber spinning using asphaltene	1	
# commercial BBC products	0	1	

Fibers from blends of as-received asphaltene and polyacrylonitrile (PAN) were processed. Based on the limited batch stabilization and carbonization trials, carbon fibers in the diameter range of 8 to 21 µm, tensile strength in the range of 0.4 to 1.1 GPa, and tensile modulus in the range of 57 to 181 GPa were made. Please see attached report at the end of this document for further details.

- **Project Outputs**

The Project results will be included as a chapter in graduate student's thesis and a potential journal publication from the project is expected.

H. BENEFITS

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

- **Economic:**
    - Commercialization of the technology to make carbon fibers from blends of asphaltene and polyacrylonitrile (PAN), at relatively low cost, will result in light weighting of automobiles and other products.
    - Studies conducted also open up avenues to use the low-cost asphaltene as a filler in thermoplastic fibers and composites.
    - Functionalization of asphaltenes is a viable route to expand its solubility in organic solvents. This expansion points towards the development of further commercial opportunities and applications.
- **Environmental:**
    - While the environmental impact was not studied as a part of the current project, light weighing of automobiles based on the technology developed under this program should lead to significant environmental benefits.
- **Social:**

    Scale up and commercialization of the outcomes of this study could result in the entrepreneurial ventures in the following areas leading to employment opportunities:

    - Low cost carbon fiber.
    - Expanded asphaltene solubility window based on functionalized asphaltenes.
    - Development of low-cost thermoplastic composites and fibers using asphaltenes as filler.

- **Building Innovation Capacity:**
    - Project aids in training of high quality skilled personnel (HQSP) about the fundamentals of asphaltene, its solubility, chemical modification, fiber spinning by blending with a variety of polymers including thermoplastics, carbon fiber processing, and the related myriad of applications.
    - Outcomes of the studies conducted in this project can lead to commercialization of various technologies and promote the start of various business ventures, as outlined in the above sub-sections.

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

Please see the attached report at the end of this document.

J. KNOWLEDGE DISSEMINATION

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

Project results will be included as a chapter in graduate student's thesis. A potential journal publication from the project is expected. A report to the Asphaltene Sample Bank has been prepared. The knowledge gained from this Project may open up new areas of exploration for combining low cost asphaltenes and PAN to make a lower cost carbon fibre. The lower cost fibre would have strong uptake across industry enabling expanded use of carbon fibre.

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

Please see the attached report at the end of this document.

Manufacturing of Carbon Fibers from Alberta Asphaltene

Public Final Report

Prepared for

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Casey Smith, Graduate Student
Dr. Kishor Gupta, Senior Research Scientist
Dr. Satish Kumar, Professor *(PI)*

Table of Contents

Executive Summary

This study has been conducted on solid asphaltene (Asp, sample S1) received from Alberta Innovates. Asp was functionalized in nitric acid. Nitric acid functionalized asphaltene (referred to as f-Asp) were characterized by FTIR and MALDI. f-Asp were found to be soluble in dimethyl acetamide (DMAc) and formed homogenous blends with polyacrylonitrile (PAN). f-Asp were further treated with methanol and characterized but were not used for fiber spinning in this study. f-Asp/PAN were spun from their solutions in DMAc, with Asp/PAN ratios in the range of 30/70 to 60/40. f-Asp blend precursor fibers in the diameter range of 16 to 77 µm, exhibiting tensile strength in the range of 197 to 361 MPa, and tensile modulus in the range of 7 to 11.7 GPa, were processed. Based on the limited batch stabilization and carbonization trials, carbon fibers in the diameter range of 8 to 21 µm, tensile strength in the range of 0.4 to 1.1 GPa, and tensile modulus in the range of 57 to 181 GPa were made. Fibers were characterized using wide angle x-ray diffraction (WAXD) and scanning electron microscopy (SEM), and exhibited good circularity. Both WAXD and SEM show random presence of significant inorganic impurity. It is expected that this impurity negatively effects fiber mechanical properties. Nonetheless, this study suggests that asphaltene based fibers when manufactured using continuous stabilization and carbonization can exhibit reasonable mechanical properties from Asp/PAN blends, for a number of applications.

In order to prepare Asp blends in polyacrylonitrile (PAN) polymer for fiber spinning, initially attempt was made to dissolve Asp in dimethyl acetamide (DMAc), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). However, this particular Asp was not fully soluble in these three solvents. Attempt was then made to prepare Asp/PAN blend solutions in DMAc/toluene, DMF/toluene, and DMSO/toluene solvent mixtures in various solvent ratios. All, these solutions exhibited phase separation, and were not suitable for fiber spinning. Asp was found to be soluble in toluene. Results of the solubility studies are presented in Appendix A.

Given Asp solubility in toluene and considering that polystyrene (PS) is also soluble in toluene, fiber spinning was attempted from Asp/PS/toluene blend solutions. While the fibers could be formed from these blend solutions, Asp/PS blends in toluene resulted in phase separated system. Asp/PS (60/40) blend precursor fibers were made in the diameter range of 46 to 82 µm and exhibiting tensile strength in the range of 6 to 11.5 MPa, and tensile modulus in the range of 0.8 to 1.4 GPa. Based on the preliminary stabilization studies, these fibers were deemed not suitable for carbonization. Asp/PS studies are presented in Appendix B.

Attempt was made to use toluene as a plasticizer for Asp, and DMAc as a plasticizer for PAN, to promote Asp/PAN melt compounding. Different levels of Asp and PAN plasticization was done, and Asp/PAN blends were melt extruded in the temperature range of 115 to 170 ºC. While this approach may hold some promise, the fibers produced in this study were not of good quality. These studies are presented in Appendix C.

Asp/polypropylene (PP) melt blending, and fiber extrusion was attempted without the use of plasticizer. Fibers containing 20, 40, 60, 80, and 100% asphaltene could be melt extruded in the temperature range of 220 to 240 ºC. These fibers had a diameter in the range of 36 to 62 µm and exhibited tensile strength in the range of 235 to 11 MPa, and tensile modulus in the range of 5.3 to 0.6 GPa. Given that the PP fiber containing 20 wt% Asp exhibited a modulus of 5.3 GPa suggests that asphaltene can be used as a low-cost filler in thermoplastic polymers in general, and in fibers such as PP in particular. Asp/PP fibers may be used for concrete reinforcement and other applications. Asp/PP (and other thermoplastics such as polyethylene) fibers may be used for stabilization and carbonization but will require further work. Asp/PP studies are presented in Appendix D.

1. Introduction

1.1. Sector introduction

Asphaltenes have sometimes been defined by their solubility in toluene or their insolubility in heptane or hexane. Previous literature proposed different structures for asphaltene [1,2]. The general consensus is that asphaltenes are composed of polycyclic aromatic molecules in the core with aliphatic chains on the ends. These aromatic molecules tend to stack up to form aggregates. Successful oil extraction and transport depends on preventing asphaltene precipitates from damaging piping and equipment by maintaining its solubility in crude oil [3,4].

Asphaltene has been studied for its potential as a carbon fiber precursor. They were either melt-spun or solution-spun using toluene, and the resulting fibers were stabilized and carbonized [5]. Carbon fibers with (a) tensile strength in the range of 0.8 – 1.1 GPa when pyrolyzed at 1000 °C [6] and (b) with tensile strength of 1 GPa and modulus of 350 MPa [7] were obtained by converting asphaltenes from coal-tar into mesophase pitch through pre-treatment followed by melt spinning and pyrolysis. Melt spun coal derived asphaltene with styrene-ethylene-butylene-styrene when carbonized at 1000 °C yielded carbon fibers with a tensile strength in the range of 0.6-1.1 GPa [8]. Solution of asphaltene in toluene were electrospun to study their potential as membranes [9]. Asphaltenes were melt-spun, treated with nitric acid, stabilized, carbonized at 800 °C and activated to produce porous carbon fibers [10].

1.2. Knowledge or Technology gaps

To the best of our knowledge, there are no prior studies on solution or gel spinning of asphaltenes with polyacrylonitrile (PAN). PAN is the most widely used precursor for the production of carbon fibers. Previously our research group has reported processing of high molecular weight PAN through gel-spinning to obtain high strength and high modulus carbon fibers [11]. Renewable carbon fiber precursors including lignin and cellulose nanocrystals have also been gel-spun and converted into carbon fibers by blending them with PAN[12,13].

To begin with, the objective of this study was to find conditions to prepare blends of asphaltenes and PAN in solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), or dimethyl sulfoxide (DMSO) that have been used for solution or gel spinning of PAN fibers. Based on the solubility parameters reported in the literature, asphaltene solubility in DMAc or DMF is expected [14]. However, experimentally, it was found that as received asphaltene (sample S1, referred to as Asp) did not fully dissolve in these solvents, and instead created a suspension [Appendix A]. Toluene dissolved the as received asphaltene, but it does not dissolve PAN. To enhance asphaltenes solubility in DMAc, controlling their dispersion or aggregation was studied from the perspective of creating functional groups on asphaltenes [15,16]. Asphaltenes have been chemically functionalized using ozone [15,17], nitric acid, and sulfuric acid [16,18]. Nitric and sulfuric acid functionalization has also been used for carbon nanotubes [19,20]. In this study, functionalization in nitric acid was chosen over sulfuric acid, as it will result in the addition of polar groups that improve the compatibility of asphaltenes with polar solvents and polymers, and removes peripheral alkyl groups without increasing the sulfur content [16].

Nitric acid functionalized asphaltenes are soluble in DMAc and form a homogeneous solution in PAN/DMAc. We consider this a significant finding, and the nitric acid functionalized asphaltenes are referred to as f-Asp. f-Asp were characterized through various techniques to identify the changes in the molecular structure and the resulting dissolution in DMAc. We further blended f-Asp (Mw: ~ 1200-1400 g/mol) with high molecular weight PAN (Mv: 500, 000 g/mol) for solution spinning into precursor fibers followed by stabilization and carbonization to yield carbon fibers. Blends of f-Asp/PAN were successfully used to produced precursor fibers over three spinning trials. The precursor fibers were further stabilized and carbonized through different protocols. Mechanical and structural characterization of the precursor and carbon fibers was performed. Two-step functionalization of asphaltenes (referred to as f1-Asp) in nitric acid followed by functionalization in methanol was also studied. However, f1-Asp were not used for spinning fibers in the current study but are considered potential promising candidates for future studies.

2. Experimental

2.1. Materials

Alberta oil asphaltenes (sample S1), a solid powder (referred to as Asp), was provided by Alberta Innovates. Based on the safety data sheet (SDS), this sample is a 'mixture of (water) poly-aromatics & other hydrocarbons containing carbon (C), hydrogen (H), nitrogen (N), oxygen (O), Sulfur (S) and traces of metals.' On a dry material basis, as per SDS, it is a mixture of polycyclic hydrocarbons with approximate following content: C 70-79%, H 7-8%, N 1.26-1.4%, S 7-8%, O 1.4-1.6%. Poly(acrylonitrile-*co*-methacrylic acid) (PAN; viscosity average molecular weight, Mv: 500, 000 g/mol; 4% MAA content) was obtained from Japan Exlan, Co. Dimethylacetamide (DMAc) and nitric acid (HNO_3) purchased from Sigma Aldrich and methanol from VWR Chemicals, were used as received.

2.2. Functionalization of asphaltenes

10 g of as received asphaltene powder (Asp) was added to a 1 L round bottom flask along with 250 mL of nitric acid and 250 mL of de-ionized water (DIW). A stirrer was added to the flask before setting up a reflux using a condenser and circulating water. The round bottom flask contents were refluxed at 120°C for 1, 2, 3, 6, 12 and 24 h. After functionalization, the contents were filtered and washed with DIW until a neutral pH of 7 was reached. The nitric acid functionalized asphaltenes were labeled as f-Asp. Asphaltene (2 h f-Asp) was used for spinning fibers, and then converting them to carbon fibers.

f-Asp was further functionalized using methanol. Figure 1 shows the reaction mechanism of transesterification process that is predicted to occur when nitric acid functionalized asphaltene is further functionalized in methanol in the presence of an acid catalyst. Previous literature used supercritical methanol (at 250 °C) to perform esterification on naphthenic acids in raw crude oil [[21]]. However, high temperature is likely not required here, as the f-asp is already oxidized. 10 g of washed and dried asphaltene from the 1h nitric acid functionalization (f-Asp) was added to a 1 L round bottom flask along with 500 mL of methanol and 2 mL of nitric acid. A stirrer was added to the flask before setting up a reflux using a condenser and circulating water. The round bottom flask contents were refluxed at 60°C for 24 hours. After functionalization, the contents were filtered and washed with DIW until a neutral pH of 7 was reached. The methanol functionalized asphaltenes were labelled as f1-Asp. f1-Asp was not used in this study to spin fibers but is considered potentially a viable system for future studies.

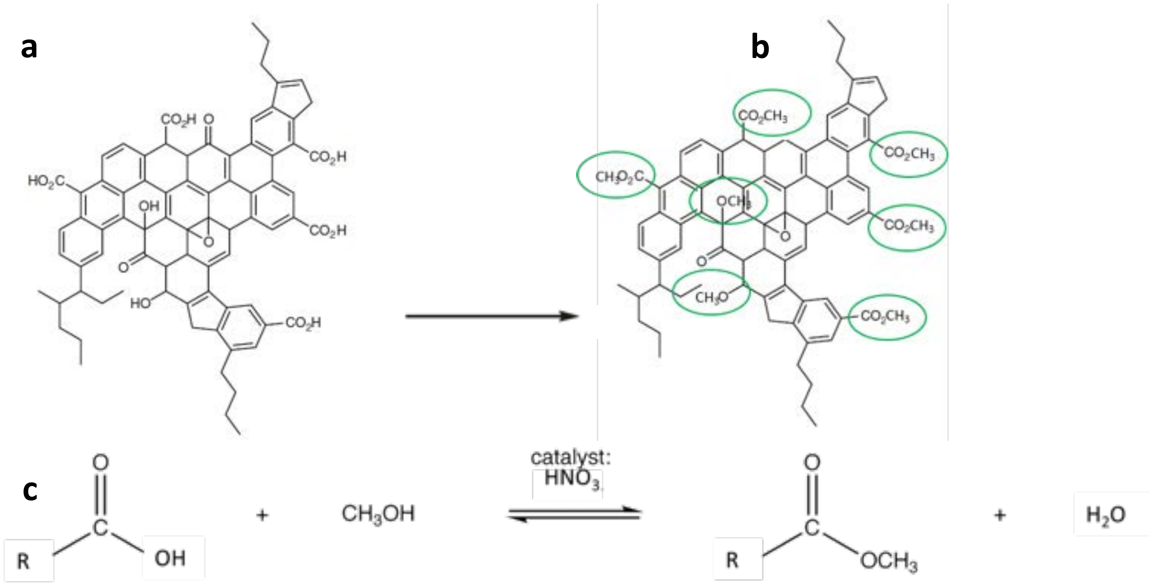


Figure 1. (a) Structure of oxidized asphaltene [22] after nitric acid functionalization. (b) Structure of methanol functionalized asphaltene (c) Predicted reaction mechanism for transesterification of oxidized asphaltene in the presence of nitric acid.

2.3. Spinning f-Asp/ PAN blend fibers

Three fiber spinning trials (referred to as trials A, B, and C) were conducted using the f-Asp/PAN blends. Spinning system by Hills Inc. (Figure 2) was used to produce the precursor blend fibers. The Hills system has two solution barrels which house the spinning solutions and the pistons (controlled by rotor) that push the solutions through the spin pack (consisting generally of filter, solution distribution plates and spinneret). In a typical dry spinning, the jet is extruded from the spinneret into air before being collected on a spool while in dry-jet wet spinning (Figure 2b), the solution passes through an air gap before going through a coagulation bath to form fibers. The fibers were spun using dry-jet wet spinning.

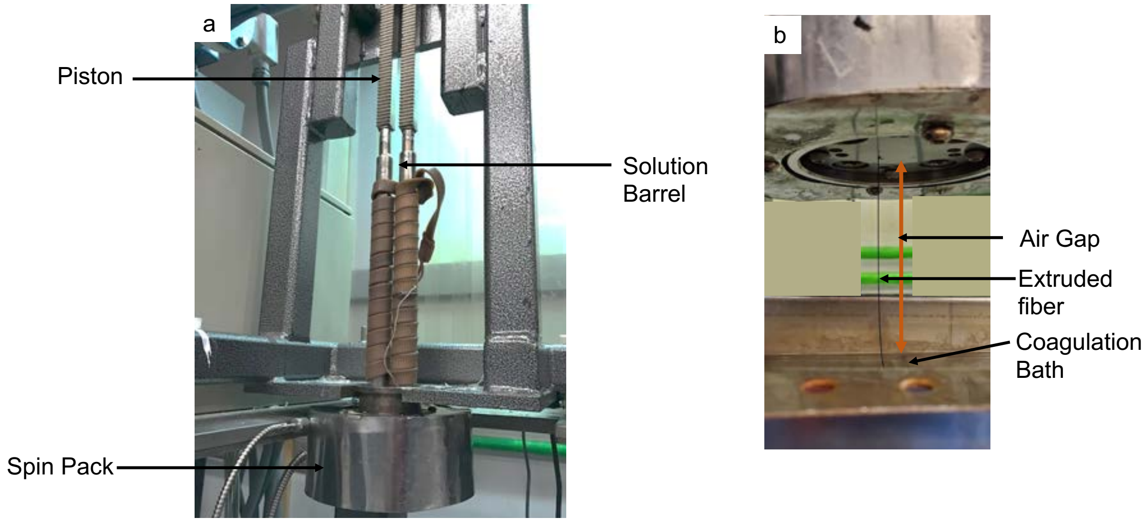


Figure 2. (a) Spinning system used for conducting the spinning trials, (b) Extruded fiber shown in the air gap during dry-jet wet spinning.

In Trial A, bi-component fibers with two different spinning solutions for the core and sheath were prepared. Core solution was made by adding 17.25 g of f-Asp powder and 11.5 g of PAN powder in 100 mL of pre-chilled (~ 0 ºC) DMAc. f-Asp/PAN/DMAc slurry was gradually heated to 90 ºC in a silicone oil bath while being continuously stirred at 200 rpm. Upon reaching the temperature of 90 ºC, it was brought down to 70 ºC and stirred for 2h. This solution was degassed in vacuum at 70 ºC and had a pasty texture. After degassing, the solution was loaded into the spinning barrel. For the sheath solution of PAN, a slurry of 11.5 g PAN in 100 mL of pre-chilled (~ 0 ºC) DMAc was first prepared in a glass reactor. The slurry was then heated to 90 ºC using a silicone oil bath and stirred at 200 rpm for 2 h. The solution was then degassed in vacuum at 70 ºC and poured into the barrel of the spinning system.

For Trial B, 7.7 g of f-Asp was added to 15 mL of DMAc and then stirred at room temperature. In a glass reactor, 18 g of PAN was slowly added to 150 mL of pre-chilled (~ 0 ºC) DMAc. PAN/DMAc slurry was slowly heated to 70 ºC using a silicone oil bath and stirred for 2h at 200 rpm. f-Asp/DMAc solution was slowly added to the PAN/DMAc solution. Blend solution of f-Asp/PAN/DMAc was left to be heated at 45 ºC overnight, with continuous stirring at 50 rpm. Next day, the temperature of the blend solution was increased to 70 ºC and stirred for 1h. The blend solution of f-Asp/PAN/DMAc was then degassed in vacuum at 70 ºC and loaded into the spinning solution barrel.

The spinning solution for Trial C was prepared in a manner similar to Trial B. 22.5 g of f-Asp was dissolved in 45 mL of DMAc at room temperature with continuous stirring. To 100 mL of pre-chilled (~ 0 ºC) DMAc, 15.2 g of PAN was added. PAN/DMAc slurry was gradually heated to 70 ºC using a silicone oil bath and stirred for 2h at 200 rpm. Further, the f-Asp/DMAc solution was added to the PAN/DMAc solution and the temperature of the blend solution was reduced to 45 ºC. The blend was stirred overnight at 50 rpm and the temperature increased to 60 ºC the next day and stirred for 1h. Then, the solution was degassed in vacuum at 60 ºC before being poured into the barrel for spinning.

For Trial A spinning, a bi-component sheath-core fiber cross-section geometry was used, and the single component fiber geometry was used for Trials B and C. The core and sheath solutions, in the case of Trial A, were coaxially extruded through a 350 μm spinneret. The flow rates of the core and sheath solutions were 2.35 and 2 mL/min, respectively, that resulted in the core to sheath area ratio of ~72:28 For spinning Trials B and C, a 200 μm spinneret was used. The extruded filament passed through an air gap of ~ 5 cm, coagulated in a chilled methanol bath (maintained at about ~ -40 ºC) and then finally taken up on the plastic spools. In all the three trials, some leaching of asphaltenes (f-Asp) into the methanol coagulation bath was observed. These as-spun fibers were stored overnight in a chilled methanol vapor environment. As-spun fibers were then hot drawn in a glycerol bath (Figure 3) at 160 - 167 º C (Trials A and B) and at 140-148 ºC (trial C) and referred to as the precursor fibers. The spinning parameters for all the three trials are listed in Table 1, and the examples of the drawn precursor fiber spools produced are shown in Figure 4.

Table 1. Parameters used for spinning blend solutions of f-Asp/PAN in Trials A, B, and C.

Parameters	**Trial A f-Asp/PAN (43/57)** [†]	**Trial B f-Asp/PAN (30/70)** [†]	**Trial C f-Asp/PAN (60/40)** [†]
Solid Content (g/dL)	Core: 28.75 (f-Asp/PAN) Sheath: 11.5 (PAN)	16	26
Spinneret (μm)	350	200	200
Spinning Barrel temperature (ºC)	70	63	60
Spinneret temperature (ºC)	70	65	60
Viscosity at 1 rad/s (Pa.s)	Core: 38 Sheath: 254	72	64
Spin draw ratio (SDR)*	0.4 – 0.6	3	1.5
Hot draw ratio (HDR)	8	6	4
Total Draw ratio (TDR)*[#]	3.2 – 4.8	18	6
Precursor fiber designation	A-P	B-P	C-P

[†] *Components in the blend are represented in terms of their weight %: f-Asp/PAN (wt. %/ wt.%).*

**For Trial A – the fibers were collected over a range of collection speeds and hence the SDR and TDR are also reported as a range.*

[#] *TDR= SDR * HDR.*

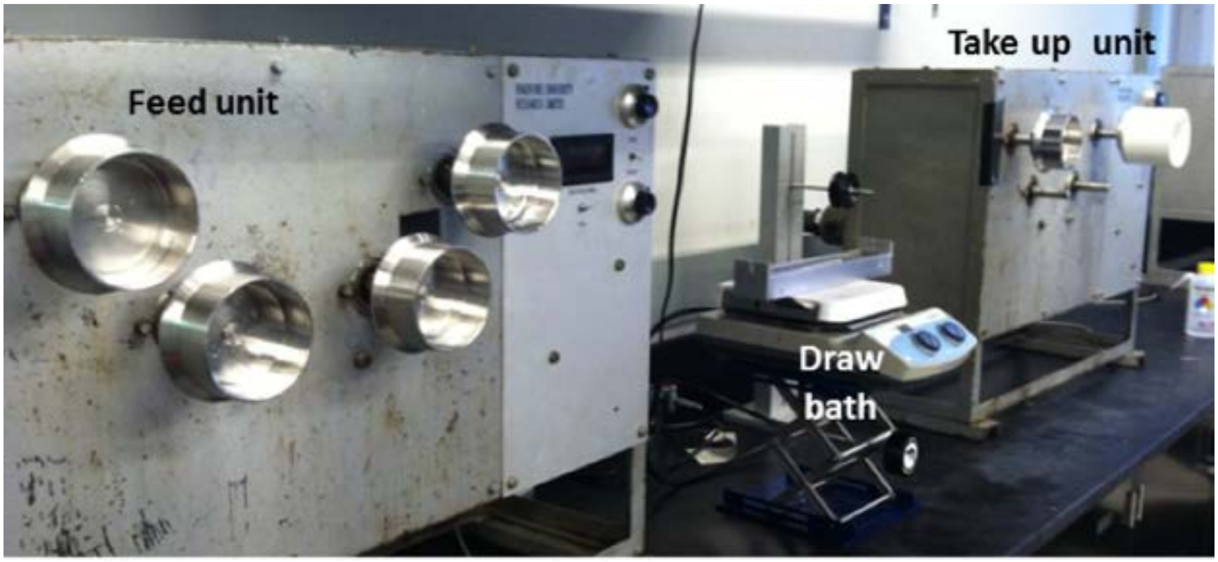


Figure 3. Experimental set-up for hot drawing of the as-spun fibers. The as-spun fibers were mounted on the feed rollers, are then passed through the glycerol draw bath, and then finally collected on the take-up rollers.

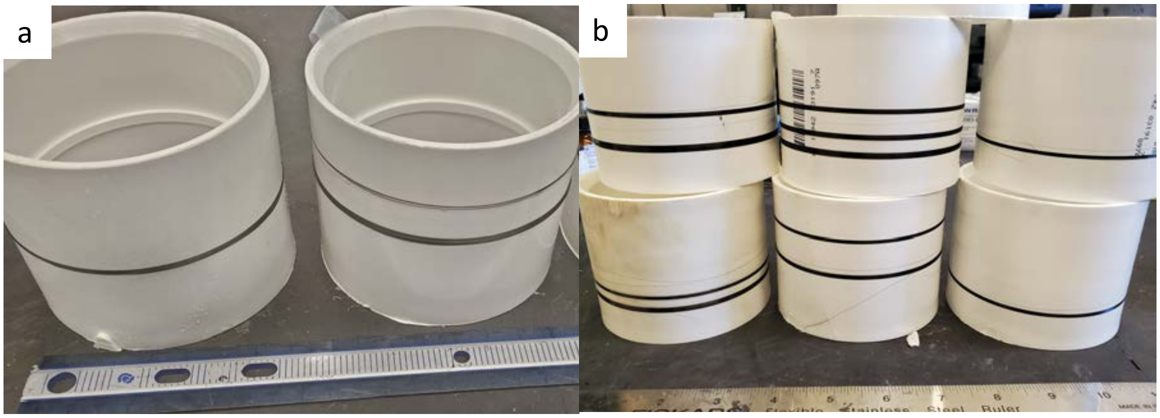


Figure 4. Representative drawn precursor fibers: (a) Fiber A-P, (b) Fiber C-P.

2.4. Stabilization and carbonization

In a tube furnace (Figure 5a; Model H17HT2.5x24, Micropyretics Heaters International, Inc), precursor blend fibers of f-Asp/PAN from the three trials (A-P, B-P, C-P) were stabilized in air and carbonized in nitrogen. The stabilization and carbonization protocols are summarized in Table 2. Figures 5b-e show the representative experimental setup for the stabilization and carbonization of the precursor fibers. The hanging weights connected to every fiber bundle was used for applying tension during these processes.

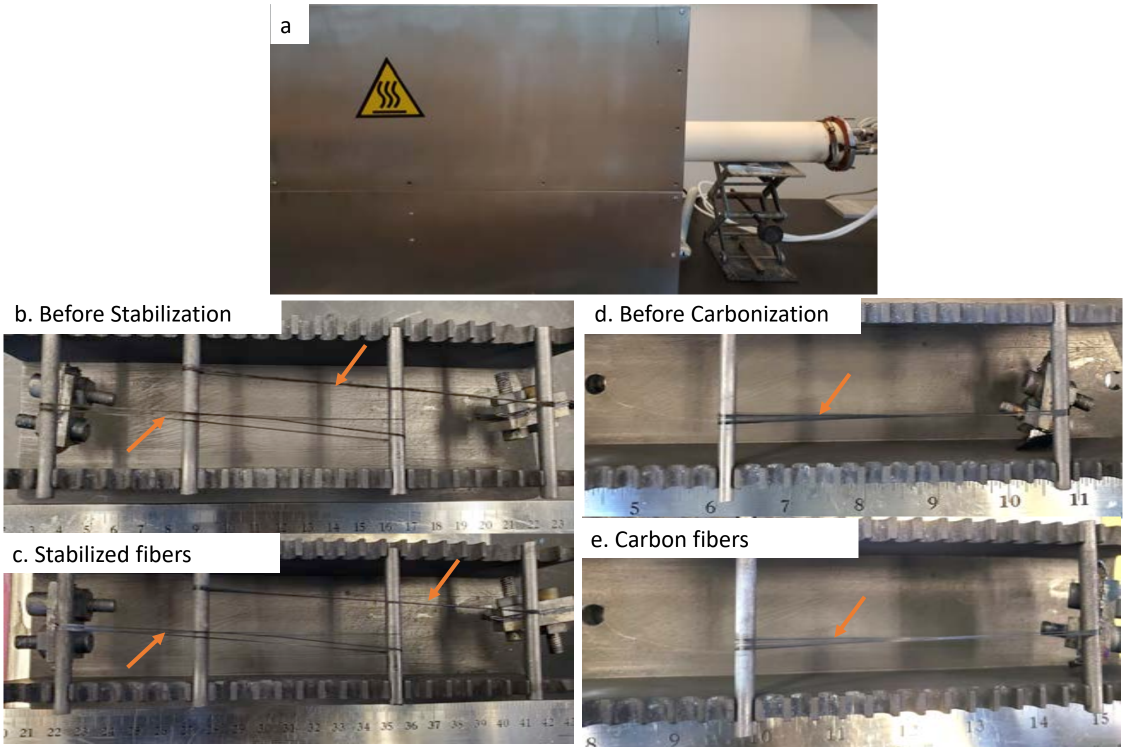


Figure 5. (a) Tube furnace used for stabilization and carbonization. (b) experimental setup for stabilizing the drawn precursor fibers. (c) stabilized fiber. (d) experimental setup for carbonizing the stabilized fibers. (e) resulting carbon fiber. Arrows indicate the fibers in each case (b-e).

Table 2. Stabilization and carbonization protocols.

	Trial A f-Asp/PAN (43/57)	**Trial B** f-Asp/PAN (30/70)	**Trial C** f-Asp/PAN (60/40)
Stabilization Trial 1 (in air)	**A-S1**	**B-S1**	**C-S1**
Protocol	3 °C /min from RT to 265 °C & hold for 270 min. 3 °C /min to 305 °C & hold for 30 min.	3 °C /min from RT to 265 °C & hold for 150 min. 3 °C /min to 350 °C & hold for 60 min.	3 °C /min from RT to 265 °C & hold for 170 min. 3 °C /min to 305 °C & hold for 10 min.
Tension applied (MPa)	10	7.5-15	5
Outcome	Fibers were not broken. No change in length	Fibers were broken. No change in length.	Fibers were not broken. ~8% shrinkage.
Carbonization Trial 1 (in Nitrogen)	**A-C1**	**B-C1**	**C-C1**
Protocol	5 °C /min from RT to 1315 °C & hold for 10 min.	5 °C /min from RT to 1315 °C & hold for 10 min.	5 °C /min from RT to 1315 °C & hold for 10 min.
Tension applied (MPa)	10	No tension	5
Outcome	Fibers were broken and crimped.	Fibers were not crimped.	Fibers were not broken or crimped.
Stabilization Trial 2 (in air)	*None*	**B-S2**	**C-S2**
Protocol	*None*	3 °C /min from RT to 265 °C & hold for 170 min. 3 °C /min to 305 °C & hold for 10 min.	3 °C /min from RT to 265 °C & hold for 150 min. 3 °C /min to 350 °C & hold for 60 min.
Tension applied (MPa)	*None*	10	5
Outcome	*None*	Fibers were not broken. ~10% shrinkage	Fibers were not broken. ~11% shrinkage
Carbonization Trial 2 (in Nitrogen)	*None*	**B-C2**	**C-C2**
Protocol	*None*	5 °C /min from RT to 1315 °C & hold for 10 min.	5 °C /min from RT to 1315 °C & hold for 10 min.
Tension applied (MPa)	*None*	10	5
Outcome	*None*	Fibers were broken but not crimped	Fibers were not broken or crimped.

2.5. Characterization

Rheological behavior of the f-Asp/PAN blend solutions was characterized using ARES Rheometer, in a parallel-plate configuration (50 mm plate diameter and 1 mm gap between the plates). Dynamic frequency sweeps from 0.63 rad/s to 300 rad/s were performed on the solutions at a constant strain of 1% and room temperature. Asp, f-Asp and f1-Asp were dried in vacuum at 90 °C for several days. Thermogravimetric analysis (TGA) was performed on these samples at a heating rate of 10 °C/min under a nitrogen atmosphere using a TA Instruments TGA Q500. Thermo Scientific Nicolet iS5 Spectrometer in the attenuated total reflectance (ATR) mode was used for FTIR study. The FTIR data was collected at a resolution of 4 cm^{-1} over the range of 400 to 6000 cm^{-1}.

2-5 mg of Asp, f-Asp, and f1-Asp powder samples were each mixed with 200 μL of HPLC grade toluene, and 1μL of the solution was placed on a stainless-steel target plate. Laser desorption ionization mass spectrometry was performed using a Bruker Daltonics 12T SolariX Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer. The data was collected in positive mode with an average of 24 spectra at 30% laser power and 1 million resolution. The data was smoothed to 0.05 m/z and peaks were picked using a threshold of Signal/Noise (S/N) > 10 and a minimum absolute intensity of 100,000 counts.

Tensile properties of the drawn precursor and the carbon fibers were measured on the RSA III solids analyzer, by mounting the individual filaments on paper tabs with a gauge length of 25.4 mm for the precursor fibers and 12.6 mm for the carbon fibers. Strain rates of 1 %/s and 0.1%/s for the tensile test of the precursor and carbon fibers, respectively were used. Cross-sectional and surface morphologies of the carbon fibers were imaged on a HITACHI SU8230 scanning electron microscope (SEM) (accelerating voltage of 2 kV and working distance of ~ 4 -6 mm). Wide-angle X-ray diffractions (WAXD) patterns of asphaltene powders, solutions in DMAc and fibers were obtained on a Rigaku MicroMax 002 X-ray generator (Cu Kα radiation, $\lambda = 1.5418$ Å, 50 kV and 0.6 mA) equipped with a R-axis IV++ detector.

Based on the result of solubility study reported in Appendix A, 1.85 g of Asp was added to 10 mL of DMAc and the dispersion was centrifuged at 10,000 rpm for 30 minutes. About 0.85 g of Asp sedimented, while about 1 g Asp remained in the supernatant (i.e., soluble in DMAc). Thus about 54% of as received asphaltene was found to be soluble in DMAc, and the remaining 46% was insoluble. This supernatant was used for obtaining WAXD pattern. Solutions of f-Asp and f1-Asp with concentrations of 1g/ 10 mL of DMAc were centrifuged at 10,000 rpm for 30 minutes. No sediments were obtained in these cases after centrifugation, and these solutions were further characterized using WAXD.

3. Results and discussion

3.1. Properties of the functionalized asphaltenes

The chemical structures of the as-received asphaltenes (Asp), nitric acid functionalized asphaltenes (f-Asp), and transesterified asphaltenes (f1-Asp) were studied from their FTIR spectra shown in Figure 6. Upon functionalization, f-Asp showed peaks of C═O stretching (1625–1800 cm^{-1}), C–O stretching (1000–1260 cm^{-1}), and NO_2 (1533, 1340 cm^{-1}), that were absent in Asp. The absorbance intensity of these peaks increased as the time of nitric acid functionalization increased. In addition, the spectra of f-Asp showed absorption bands at 1715 and 1005 cm^{-1}, associated with stretching and bending vibrations of ester and carboxy groups [15]. On the other hand, the intensity of the aromatic C–H peak (2850–2950 cm^{-1}) and the −CH2/–CH3 asymmetric deformation peak (1452 cm^{-1}) were reduced by nitric acid functionalization consistent with the results of Ignatenko et al. [16]. The modification of the chemical structure of the as-received asphaltenes through functionalization in nitric acid resulted in their dissolution in DMAc, and in a homogeneous solution with PAN.

f1-Asp showed reduction in the 1005 cm^{-1} peak absorbance intensity associated with stretching and bending vibrations of ester and carboxy groups in addition to an increase in the 1193 cm^{-1} and 1452 cm^{-1} peaks responsible for the O−C stretch and the CH_3 asymmetric deformation of the O−CH3 group, respectively [23]. f1-Asp was not soluble in methanol but was soluble in DMAc.

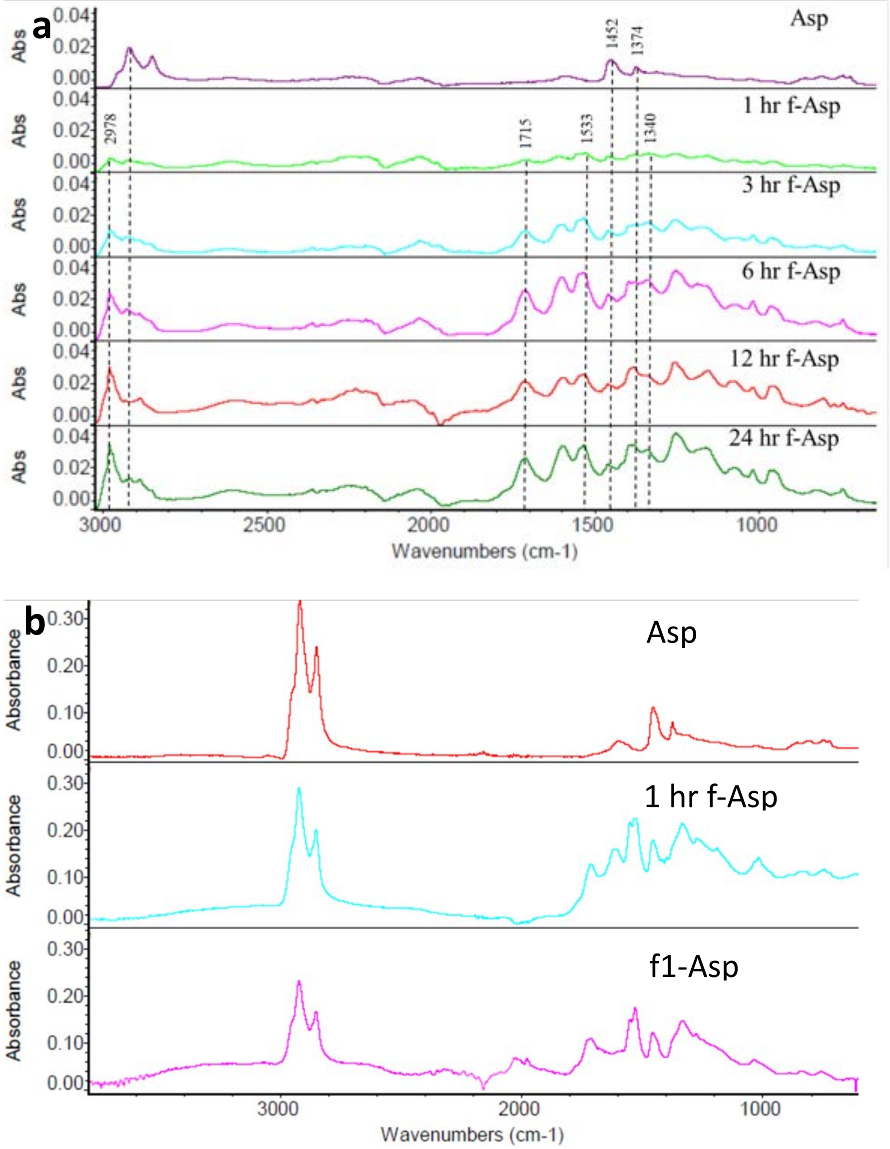


Figure 6. FTIR spectra of (a) Asp and f-asp after various times of functionalization in nitric acid and, b) Asp, f-Asp, and f1-Asp.

MALDI was used to evaluate the molecular weights of the as-received, nitric acid and methanol functionalized asphaltenes. Figure 7 shows that some degradation in molecular weight occurred during nitric acid functionalization, as Asp's molecular weight was 1402 g/mol while for 1 h and 6 h f-Asp samples, the values were 1210 and 1170 g/mol, respectively. On the other hand, the 24 h f-Asp sample had a marginally higher molecular weight of 1303 g/mol than the other f-Asp. The asphaltene after 24 h methanol functionalization showed an increase in molecular weight to 1997 g/mol, offering further evidence of successful transesterification as -OH groups were replaced with $-OCH_3$ groups.

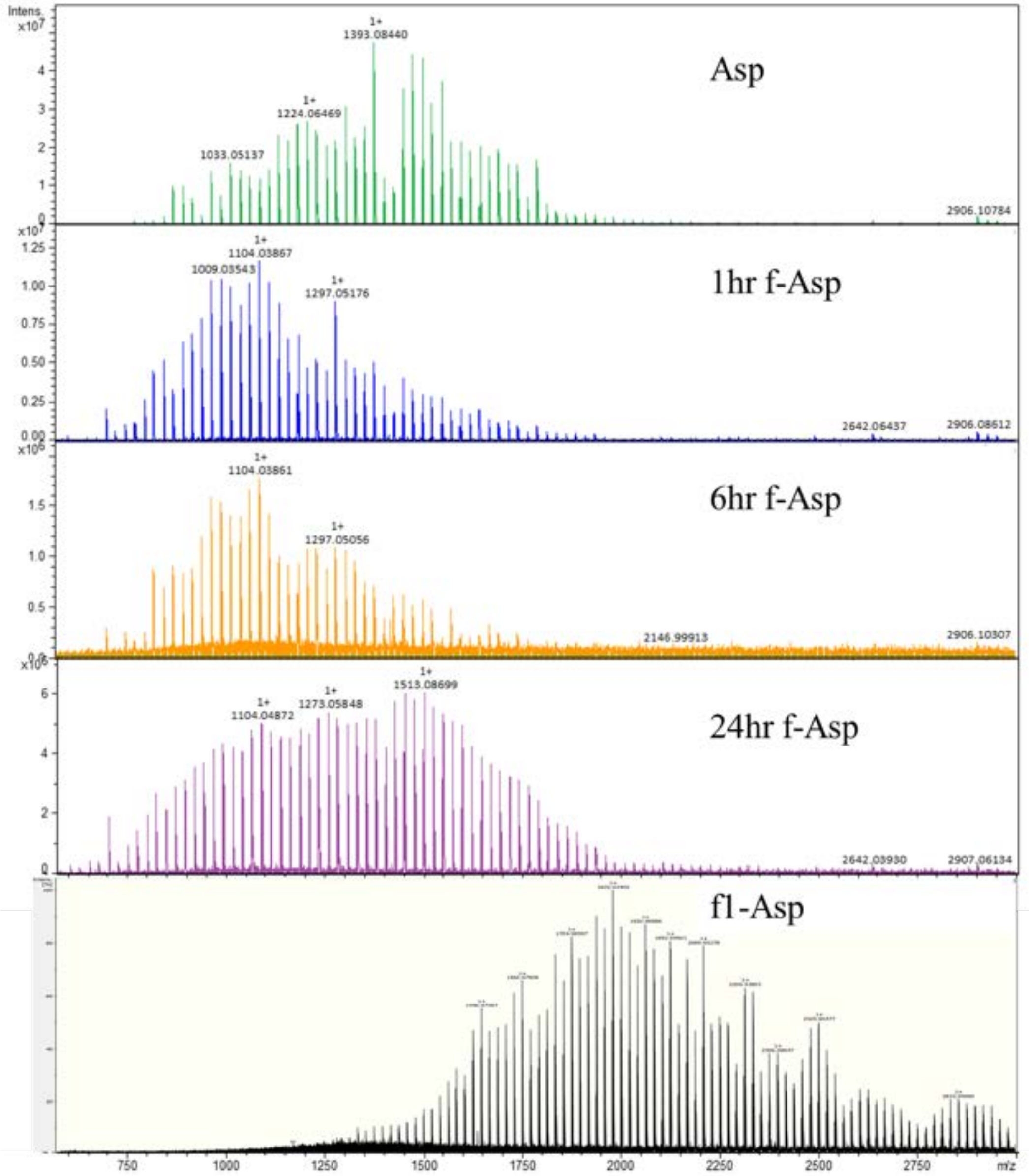


Figure 7. MALDI spectra of the as-received (Asp), nitric acid treated (f-Asp) and methanol treated (f1-Asp) samples.

Figure 8 shows the thermal degradation of Asp, f-Asp, and f1-Asp. As-received Asp lost less than 10% of the weight before 350 °C and ~ 52% of the weight between 350 and 500 °C. The degradation of all f-Asp and f1-Asp started at a lower temperature, just above 100 °C and continued steadily thereafter, due to the added functional groups. Overall, f-Asp and f1-Asp retained higher weight above 500 °C, than the Asp.

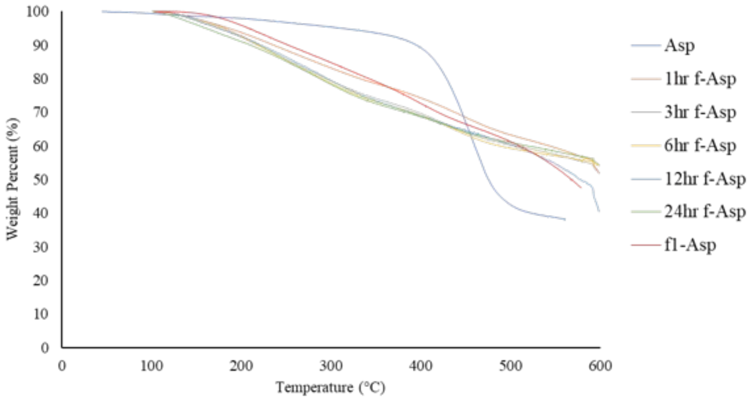


Figure 8. TGA of Asp, f-Asp, and f1-Asp samples.

Though the f1-Asp were not used in the current study for spinning fibers, they are potentially promising candidates for carbon fiber precursors in further studies. Figure 9 shows a diagram of a proposed setup for the industrial processing of functionalization of asphaltene.

The functionalization method employed in the current study needs further optimization. However, this study makes progress towards the identification of a scalable process to produce asphaltenes that are compatible with organic solvents such as DMAc and DMF.

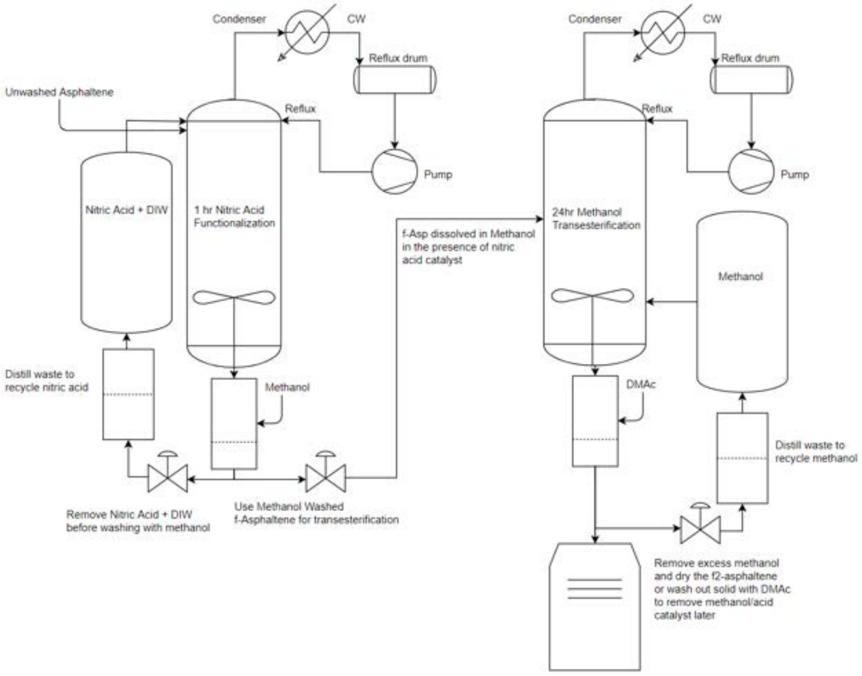


Figure 9. Diagram of proposed industrial setup for functionalization of asphaltenes.

3.2. Rheological behavior of asphaltene solutions

The terminal slope (when test frequency ω → 0) of log G′ (storage modulus) versus log G″ (loss modulus) curve, also known as a modified Cole-Cole plot (Figure 10a), can be used quantitatively to study the solution homogeneity, and a slope ~2 indicates the upper limit [24–26]. Slopes calculated for f-Asp/PAN solutions of Trials A (core solution), B, and C are 0.9, 1.5 and 1.4, respectively. Higher slope value suggests higher degree of solution homogeneity. The core solution of Trial A with the lowest slope of 0.9, was the least homogenous solution. Method of solution preparation for Trial A was different than the methods used for the other two trials. This could partly be responsible for this inhomogeneity. Figure 10b shows the complex viscosity of f-Asp/PAN and PAN solutions as a function of angular frequency.

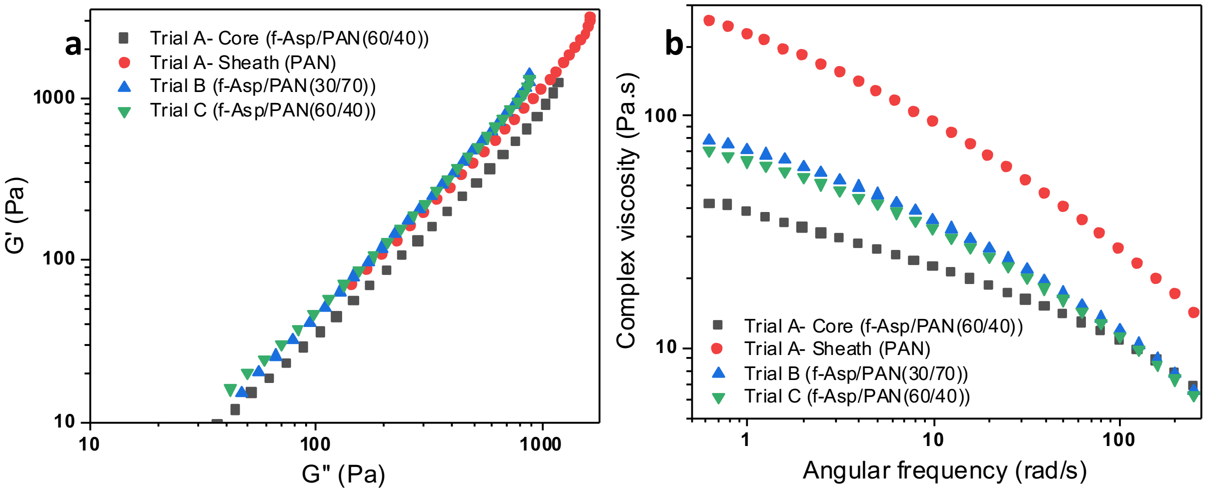


Figure 10. Rheological behavior of f-Asp/PAN blend solutions. (a) Modified Cole-Cole plot, (b) complex viscosity as a function of angular frequency.

3.3. Structural characterization of asphaltenes and their solutions

Literature reports of asphaltenes show three wide angle X-ray diffraction (WAXD) peaks at 2θ of ~11 – 20° (referred to as gamma band), ~ 26° (002 plane), and ~43° (10 plane) [27,28]. As received asphaltene powder showed all the three peaks distinctly, while the f-Asp exhibited a merged peak of the gamma band and 002 plane (Figure 11a). Figure 11b shows the WAXD scans of asphaltene solutions in DMAc. Integrated WAXD scans for the powders and solutions were obtained by subtracting the diffraction from a background of the glass capillary that was used for holding the samples for WAXD study.

The structural parameters are listed in Table 3. Interestingly, the stacking size of the aromatic clusters (L002) decreased from 2.2 to 0.8 nm upon functionalization and the solutions of asphaltenes also presented cluster sizes ~0.7 – 0.8 nm. This suggests that aromatic clustering is reduced as they are broken due to functionalization.

Another parameter, aromaticity (f_{ar}) in equation 1 is defined as the ratio of 002 peak area to that of the area of γ and 002 peaks , and is typically used to indicate the fraction of aromatic carbon in asphaltenes that are capable of stacking [29].

$$f_{ar} = \frac{A_{002}}{A_{002}+A_{\gamma}} \tag{1}$$

It is important to note that the aromaticity f_{ar} is not based on all the aromatic carbon in asphaltene but instead based exclusively on the stacked clusters aromatic carbon that contributes to the 002 peak. As-received asphaltene's aromaticity of 0.19 increased to 0.27 upon nitric acid functionalization (f-Asp). Aromaticity of f-Asp and f1-Asp further increased marginally to ~0.31-0.35 on dissolution in DMAc.

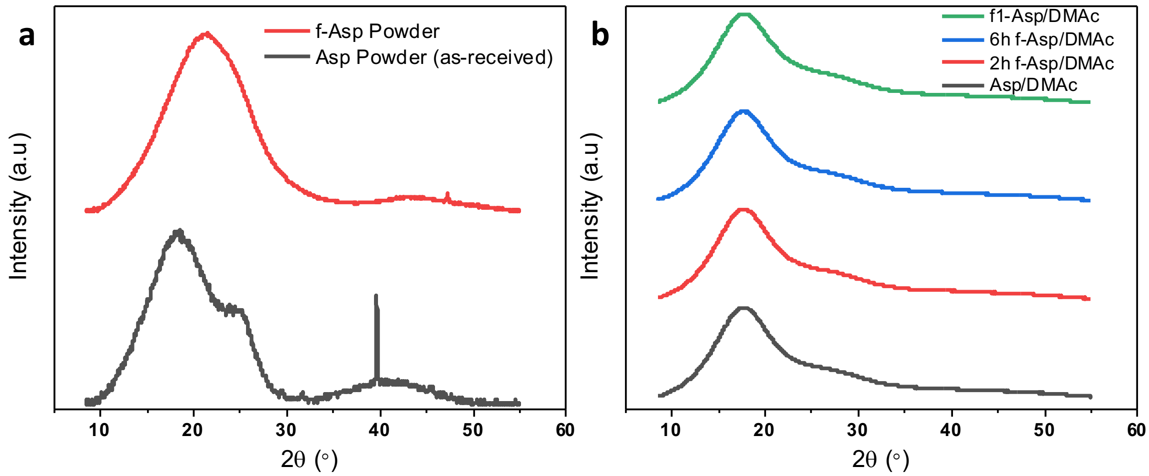


Figure 11. Integrated WAXD scans. (a) as received Asp and f-Asp powders, (b) Asp, f-Asp and f1-Asp solutions (1 g/10 mL) in DMAc. The high intensity peak at 2θ ~ 40° in Figure a has not been explained.

Table 3. Structural parameters of asphaltene powders and solutions in DMAc (1 g/10 mL).

	Asp	**f-Asp**	**Asp/DMAc**	**2 h f-Asp /DMAc**	**6 h f-Asp /DMAc**	**f1-Asp/ DMAc**
d_{γ} (nm)	0.478	0.426	0.506	0.505	0.506	0.505
d_{002} (nm)	0.354	0.366	0.347	0.347	0.349	0.352
L10 (nm)[a]	1.0	0.9	0.4	0.4	0.4	0.5
L002 (nm)[b]	2.2	0.8	0.7	0.8	0.7	0.7
f_{ar}	0.19	0.27	0.31	0.31	0.32	0.35

[a] *Crystal size of (10) plane at 2θ~ 43°, according to Scherrer's equation with K = 0.9.*

[b] *Crystal size of (002) plane at 2θ~ 26°, according to Scherrer's equation with K = 0.9.*

3.4. Mechanical properties and structural parameters of precursor fibers

The mechanical properties and structural parameters of the drawn precursor fibers were first evaluated and are listed in Table 4. The inhomogeneity of the spinning solution, as elucidated by the slope of the modified Cole-Cole plot for Trial A, was translated into the precursor fibers, as well. Consequently, amongst the three spinning trials, A-P fibers presented the largest variation in their diameters, tensile strength and modulus. A-P fibers, with the highest solid content and the larger spinneret diameter, had the highest diameter and the lowest draw ratio of the three fibers. C-P fibers with twice the asphaltene content as B-P fibers, showed 45 % and 40 % reduction in the tensile strength and modulus, respectively. Differently, A-P fibers with ~43 wt.% f-Asp overall had tensile strength comparable to the C-P fibers which contained 60 wt.% f-Asp. This is likely a result of higher degree of solution inhomogeneity in trial A. The precursor tensile modulus was also highest for trial B, and was comparable for trials A and C.

Structural parameters of the precursor fibers were influenced by the overall amount of f-Asp in the fiber (Table 4). A-P fibers with the lowest amount of amorphous f-Asp showed the highest crystallinity, crystal size, and orientation, supporting the trend of the tensile modulus. Ratio of the d-spacing of 2θ ~17° and 30° peaks of PAN ($d_{17°}/d_{30°}$), closer to 1.732, indicates a hexagonal packing structure of the PAN crystal in all three cases [30]. Thus, addition of f-Asp to the blend did not significantly alter the PAN crystal structure.

PAN's characteristic WAXD peaks at 2θ ~17° and ~30° are present in all the three precursor fibers as expected (Figure 12 and 13). A-P also showed a peak at 2θ ~13° (d-spacing: 0.671 nm) with no preferential orientation and appears to be characteristic of the asphaltene gamma band (2θ ~11-20°, d-spacing ~0.5 nm) than arising due to PAN. This peak is absent in the B and C precursor fibers. This is likely due to the phase separation of f-Asp and PAN, as evidenced from the non-homogeneity of A-P fibers.

Table 4. Mechanical properties and structural parameters of various drawn precursor fibers.

	A-P f-Asp/PAN (43/57)	**B-P f-Asp/PAN (30/70)**	**C-P f-Asp/PAN (60/40)**
TDR	3.2 - 4.8	18	6
Diameter (μm)	77 ± 7	15.7 ± 0.6	31.7 ± 0.7
Tensile strength (MPa)	205 ± 44	361 ± 29	197 ± 13
Tensile modulus (GPa)	7.8 ± 1.6	11.7 ± 0.7	7.0 ± 0.5
Elongation at Break (%)	7.1 ± 0.9	6.4 ± 0.6	9.2 ± 0.6
PAN Crystallinity (%)	50	55	39
PAN Crystal size (nm)	7.9	8.6	6.7
f_{PAN}^{c}	0.75	0.78	0.55
$d_{17°}/d_{30°}^{d}$	1.728	1.727	1.722

[a] *Crystallinity is calculated by excluding amorphous contributions from both PAN and f-Asp (γ band) from PAN's crystalline peaks.*

[b] *Crystal size of PAN at 2θ ~17° (200) and (110) planes.*

[c] *Herman's orientation factor of PAN calculated from the azimuthal scan of PAN (200) and (110) planes (and adding the contribution after deconvolution of the 2θ ~17° peak from the meridional scan in the case of C-P fiber).*

[d] *Ratio of d-spacing of diffraction peaks at 2θ ~17° and ~30°*

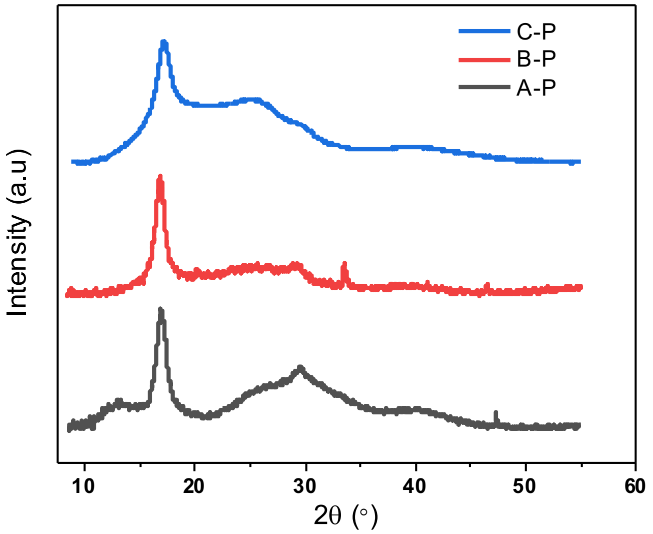


Figure 12. Integrated WAXD scans of drawn precursor f-Asp/PAN fibers, as indicated.

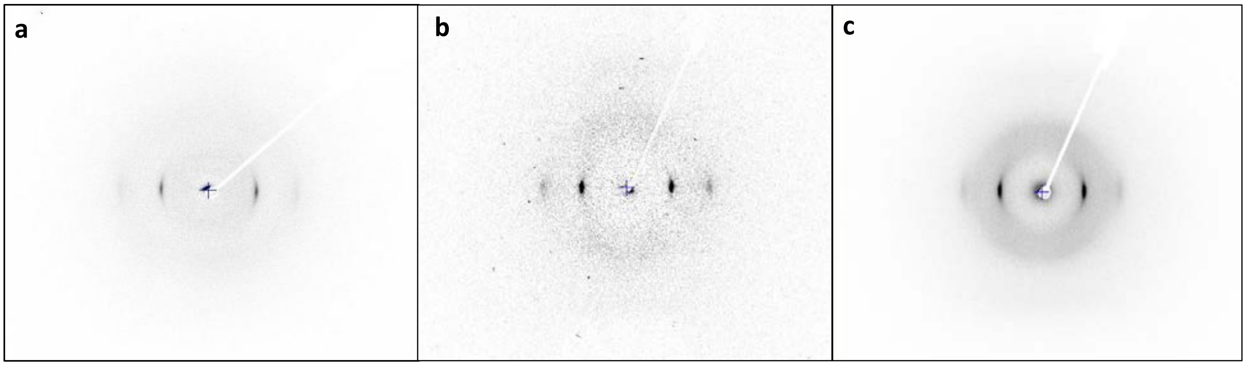


Figure 13. 2D WAXD patterns of precursor f-Asp/ PAN drawn fibers. (a) A-P, (b) B-P and (c) C-P.

3.5. Structural characterization of stabilized fibers

Common characteristics in the WAXD (Figure 14 and 15) of all the stabilized fibers, excluding A-S1 fibers, were the high intensity 2θ ~26° peak and the relatively low intensity 2θ ~43° peak. A-S1 fibers showed a strong peak around 2θ ~13°, that was also present in their precursor fibers. PAN's characteristic 2θ ~17° peak was absent in all the stabilized fibers, except the B-S2 and C-S1 fibers, where the shoulder ~16 to 18° indicated an incomplete stabilization. This is attributed to the same protocol for stabilization used in the cases of B-S2 and C-S1 fibers. The incomplete stabilization affected the properties of the resultant carbon fibers, as elucidated in the later section.

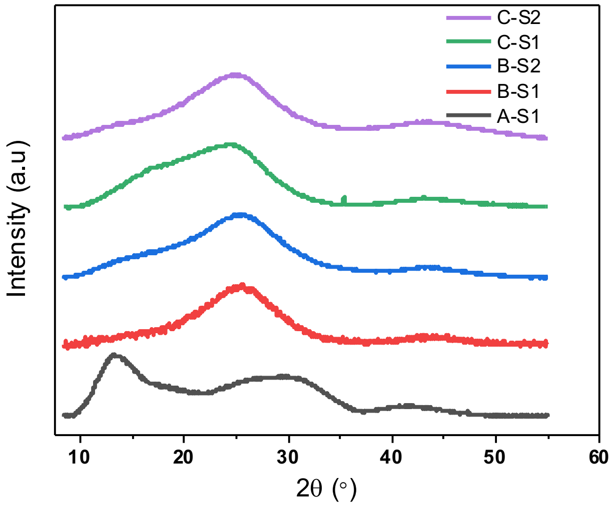


Figure 14. Integrated WAXD scans of various stabilized fibers, as indicated.

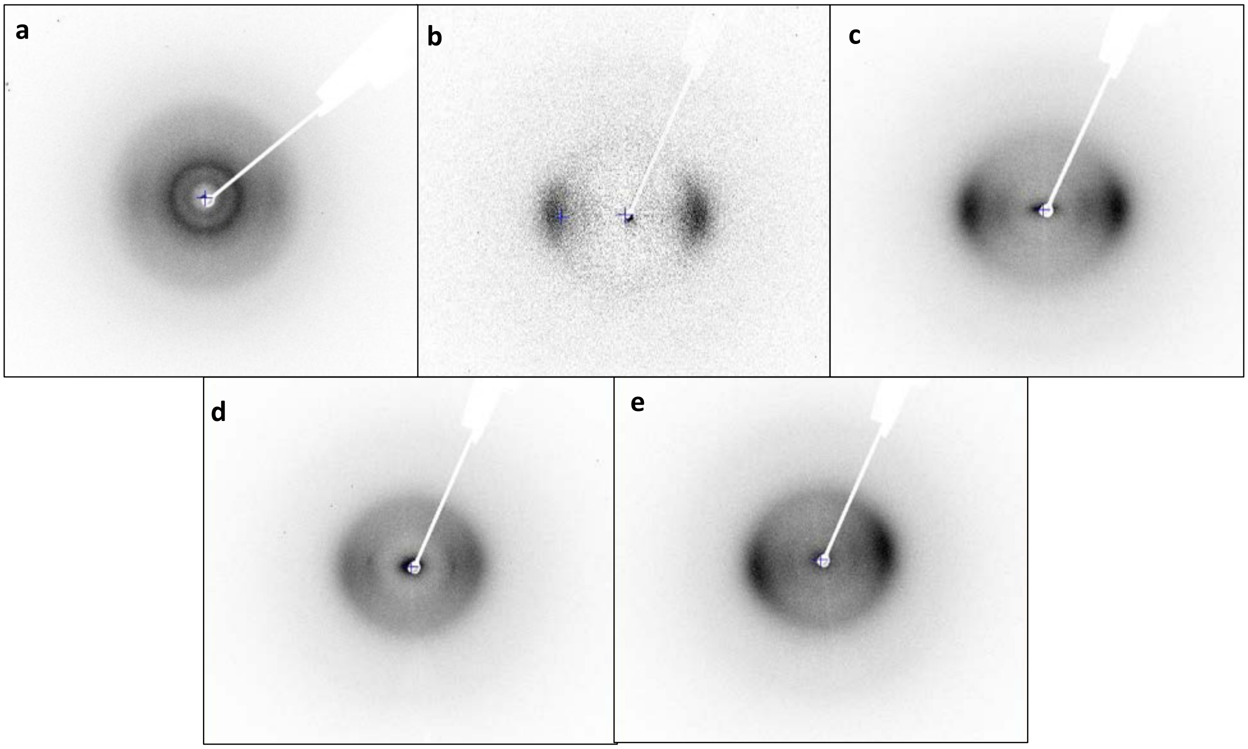


Figure 15. 2D WAXD patterns of stabilized fibers. (a) A-S1, (b) B-S1, (c) B-S2, (d) C-S1 and (e) C-S2.

3.6. Morphology of carbon fibers

SEM cross-sections of B-C1 carbon fibers did not exhibit significant porosity (Figure 16a-d). On the other hand, while certain sections of the surface were smooth and non-porous, other surface sections showed some porosity (Figure 16e-h). B-C2 carbon fiber presented morphologies similar to B-C1 (Figure 17). Pores with average diameters of 0.8 and 0.6 μm were observed in the cross-section and surface of C-C1 (Figure 18) and C-C2 (Figure 19) fibers, respectively. Porous morphology of these fibers played a role in reducing the mechanical properties of these fibers and suggest that further optimization is needed for processing these precursor and carbon fibers. Further work may also be needed in purifying and treating asphaltenes.

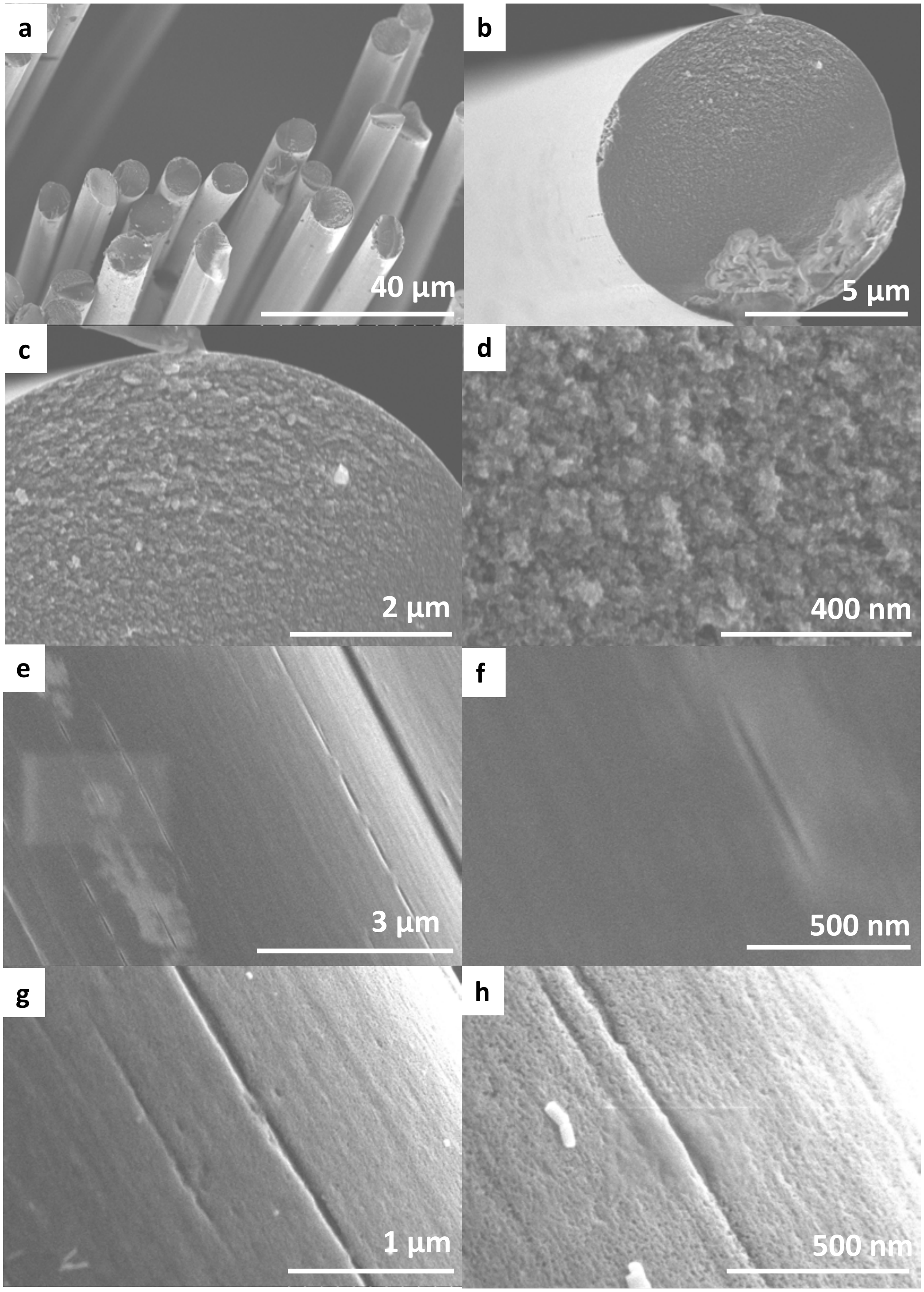


Figure 16. Cross-sectional (a-d) and surface (e-h) SEMs of B-C1 fibers.

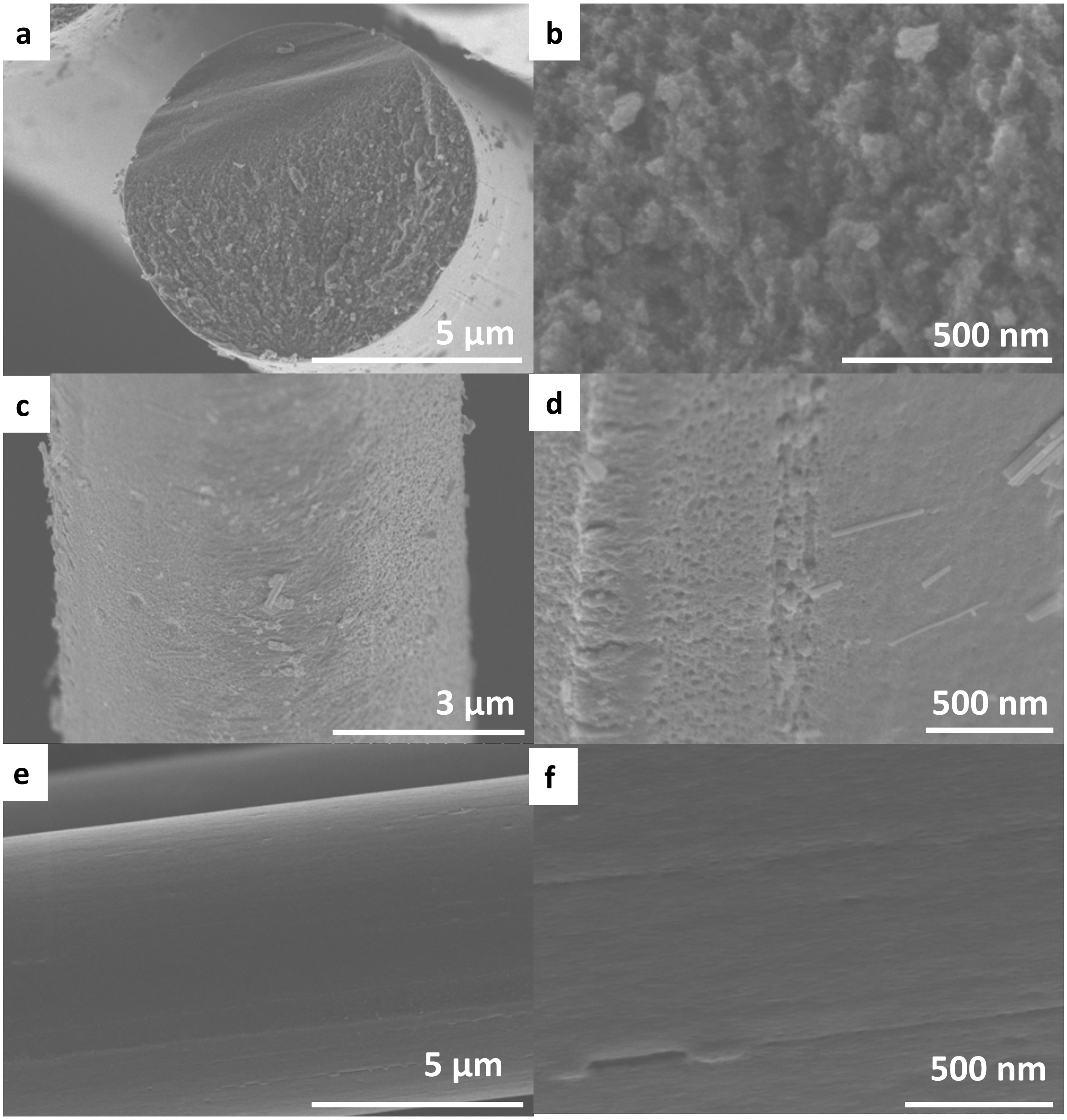


Figure 17. Cross-sectional (a-b) and surface (c-f) SEMs of B-C2 fibers.

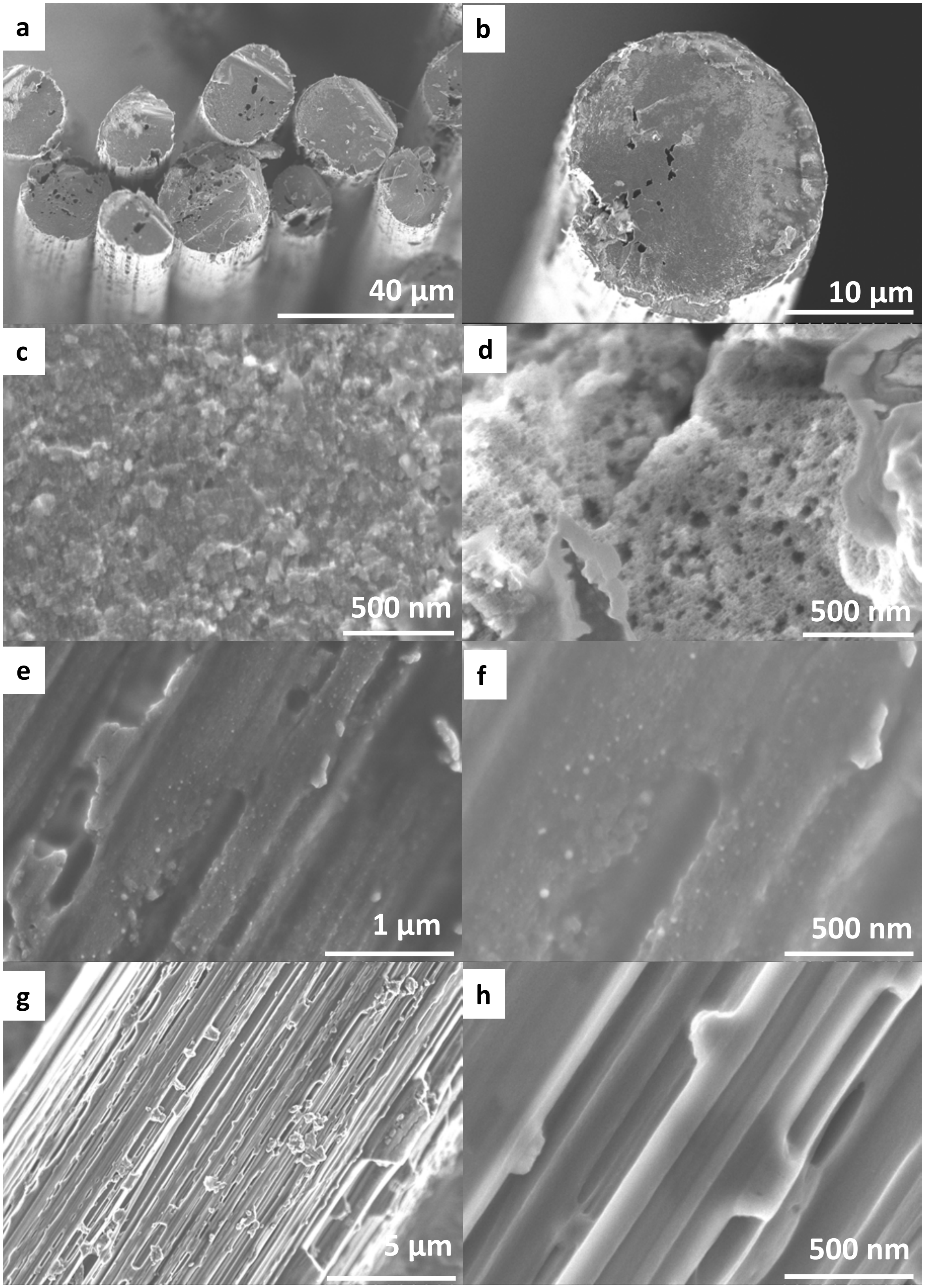


Figure 18. Cross-sectional (a-d) and surface (e-h) SEMs of C-C1 fibers.

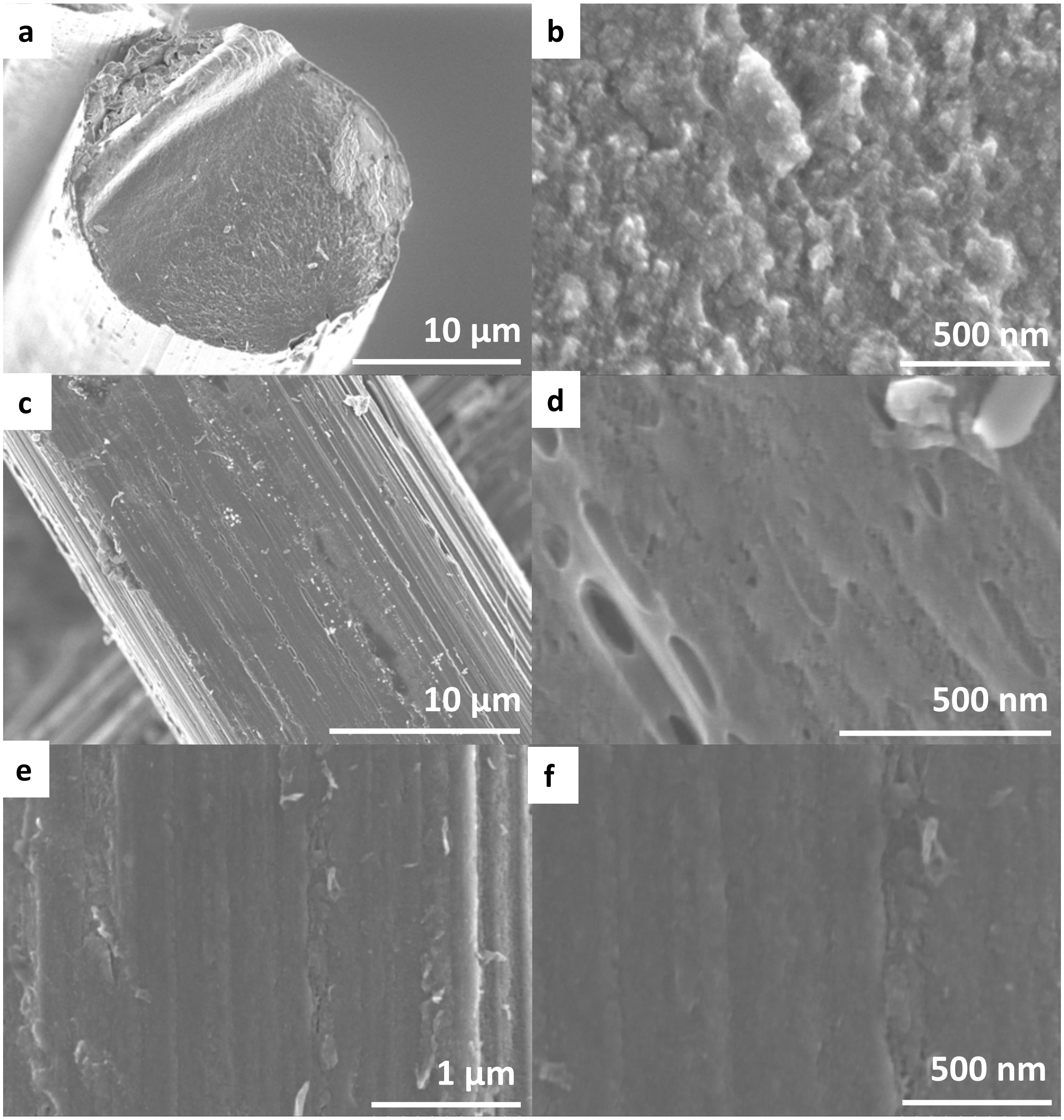


Figure 19. Cross-sectional (a-b) and surface (c-f) SEMs of C-C2 fibers.

3.7. Mechanical properties and structural parameters of carbon fibers

Carbon fibers with good structural integrity were not produced from the A-P precursor fibers. A-C1 fibers were found to be broken and crimped at the end of the carbonization, and their mechanical properties could not be measured. B-C1 fibers carbonized without tension showed higher tensile modulus than B-C2 fibers that were carbonized with tension (Table 5). This result is counterintuitive. Breakage of B-C2 during carbonization and incomplete stabilization, are probably the reasons for the decrease in modulus, despite the application of tension. C-C2 fibers had higher tensile modulus than C-C1. This is most likely due to complete stabilization in the case of C-C2 fibers rather than C-C1.

Overall better mechanical properties of B-C in comparison to C-C fibers are attributed to higher content of PAN in the B-P fibers than in C-P fibers. With a tensile strength as high as 1.1 GPa and tensile modulus as high as 181 GPa, B-C1 fibers showed the best mechanical properties of the various carbon fibers produced in this study. Carbon fibers from coal sourced asphaltenes that were converted to mesophase pitch, melt spun and pyrolyzed at 1000 °C had tensile strength in the range of 0.8-1.1 GPa [6]. Another study of carbon fibers from coal derived asphaltenes reported tensile strength of 1 GPa and modulus of 350 MPa [7]. There is further scope to improve the tensile properties of carbon fibers obtained by solution or gel spinning of petroleum based asphaltenes. Optimizing the influencing factors including tension, stabilization protocol and content of f-Asp in the blends are to be considered for improving the mechanical properties of carbon fibers from asphaltene precursors.

Table 5. Mechanical properties of f-Asp/PAN blend carbon fibers.

	B-C1 f-Asp/ PAN (30/ 70)	**B-C2** f-Asp/ PAN (30/ 70)	**C-C1** f-Asp/ PAN (60/ 40)	**C-C2** f-Asp/ PAN (60/ 40)
Diameter (μm)	8.1 ± 0.2	8.8 ± 0.2	21.5 ± 0.8	19.7 ± 0.8
Tensile strength (GPa)	1.1 ± 0.5	0.9 ± 0.3	0.4 ± 0.2	0.5 ± 0.3
Tensile modulus (GPa)	181 ± 33	133 ± 12	57 ± 14	123 ± 69
Elongation at break (%)	0.6 ± 0.3	0.7 ± 0.2	0.6 ± 0.3	0.6 ± 0.3

Characteristic WAXD carbon fiber peaks at 2θ ~26° (002) and 43° (10) were observed in all the carbon fibers produced in the study (Figure 20). BC-2 fibers distinctly revealed additional sharp peaks at 2θ ~ 21.8°, 23°, 23.5°, 25.6°, 28.7°, 33.5°, 34.1°, 35.4°, 36.9°, 40.3°, 44.9°, 48.1°, 50.2°, and 54.2° (Figure 20d). Sulfur is known to produce diffraction peaks at 2θ ~ 23.1°, 25.4°, 25.8°, 27.7°, 31.4°, 37°, and 42.8° [31,32]. Some BC-1 fibers also occasionally showed additional peaks (Figure 21). As-received asphaltenes were reported to contain ~8% of Sulfur along with trace quantities of metals. The non-carbon diffraction peaks could arise from Sulfur, trace metals, and other residual impurities remaining after pyrolysis. Some B-C1 fibers also showed particles (average diameter: 26 nm) or fibrils (average diameter: 17 nm), while the average diameter of particles and fibrils in BC-2 fibers was 61 nm (Figure 22 and 23). These particles or fibrils are most likely composed of some of the impurities and likely result in some of the WAXD peaks in these fibers. Further elemental analysis of the B-C fibers is required to isolate the source of these additional peaks and ascertain the hypothesis. Some morphological features were also occasionally found on the surface of C-C1 and C-C2 fibers (Figures 24 and 25), but they did not manifest themselves in non-carbon WAXD peaks (Figures 26), unlike in the case observed in B-C fibers.

B-C1 fibers showed higher orientation of the turbostratic graphitic planes than the B-C2 fibers (Table 6) and resulting in higher tensile properties of B-C1 fiber in comparison to B-C2 fiber. Similarly, C-C2 fibers, had higher orientation factor, when compared to C-C1 fibers. B-C1 fibers with the highest orientation factor had the highest modulus and tensile strength amongst all the fibers.

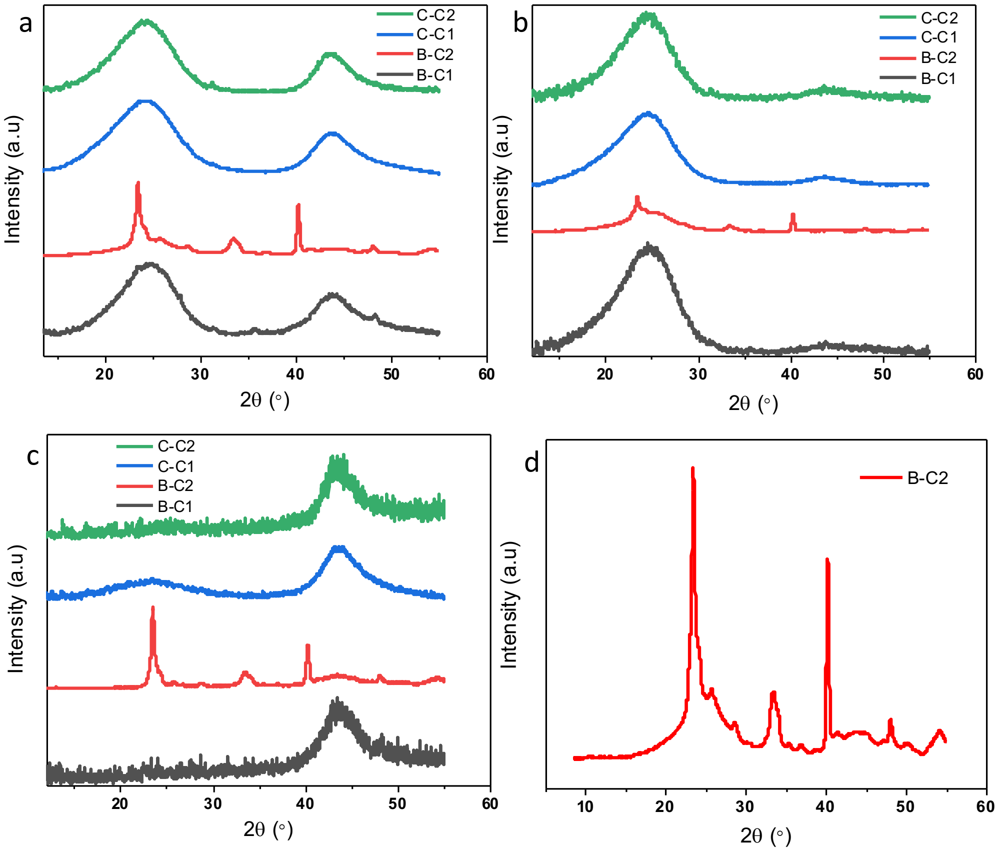


Figure 20. (a) Integrated, (b) equatorial and (c) meridional WAXD scans of various carbon fibers as indicated. (d) Integrated WAXD scan of B-C2 carbon fibers with magnified intensity.

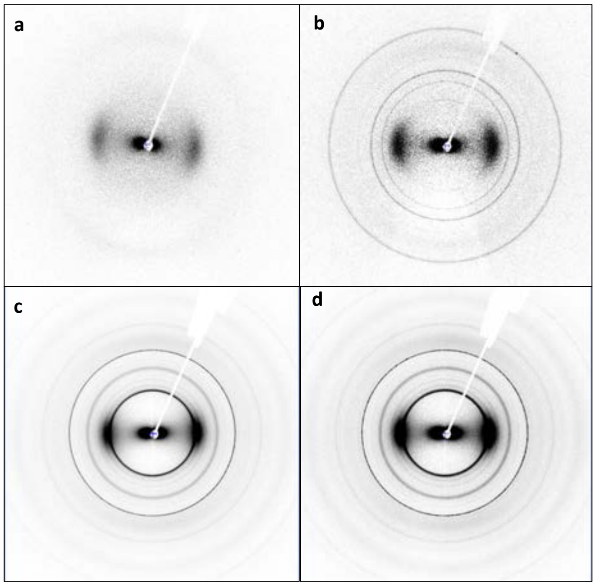


Figure 21. 2D WAXD patterns of various carbon fibers. B-C1 (a-b) and B-C2 (c-d). (a) and (b) WAXD patterns were obtained from different spots on the same sample bundle and indicate that the presence of inorganic impurities was not present everywhere in the fiber. (c) and (d) were also obtained at different spots on the same carbon fiber bundle.

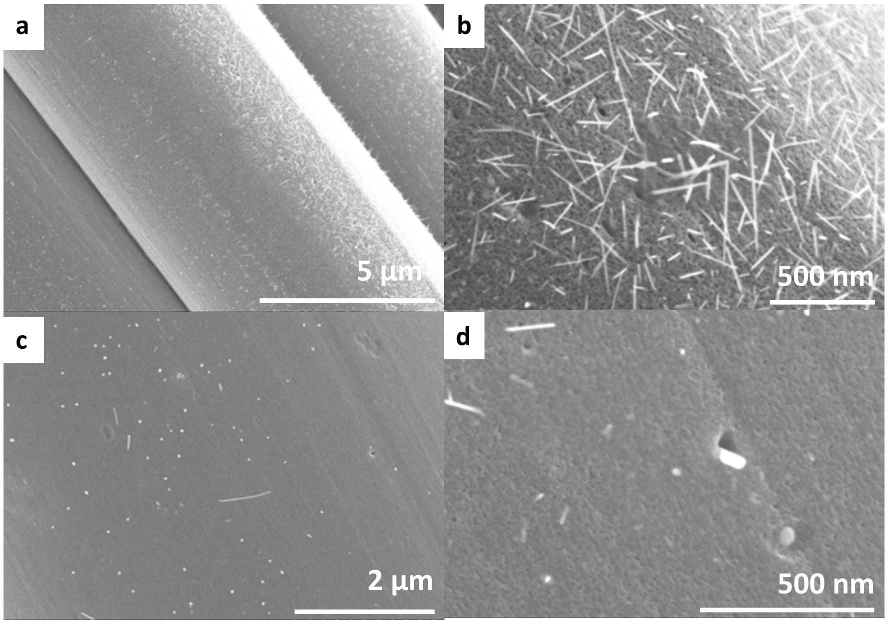


Figure 22. SEM images of the surface of B-C1 carbon fibers.

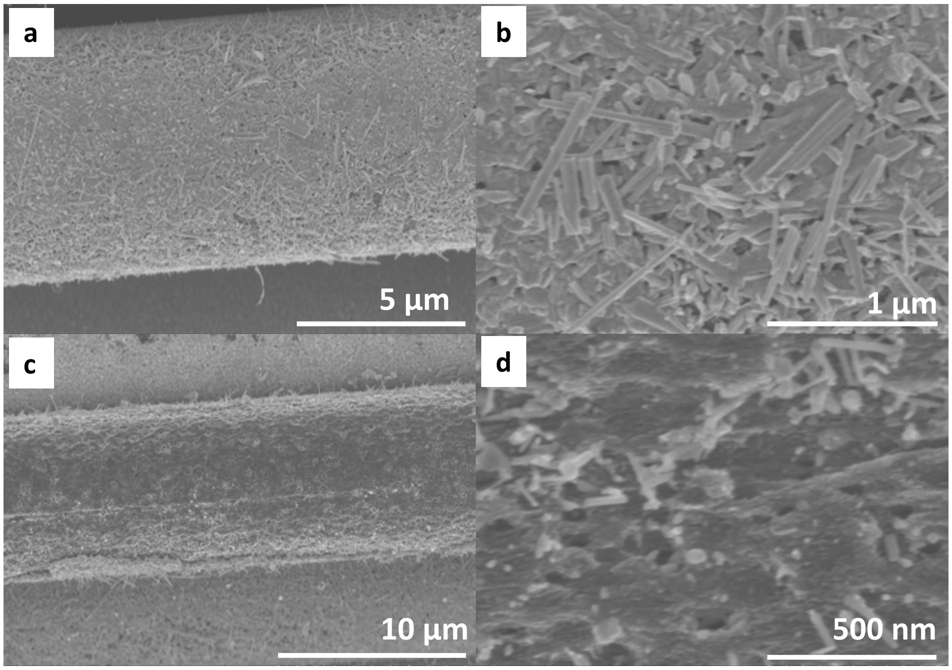


Figure 23. SEM images of the surface of B-C2 carbon fibers.

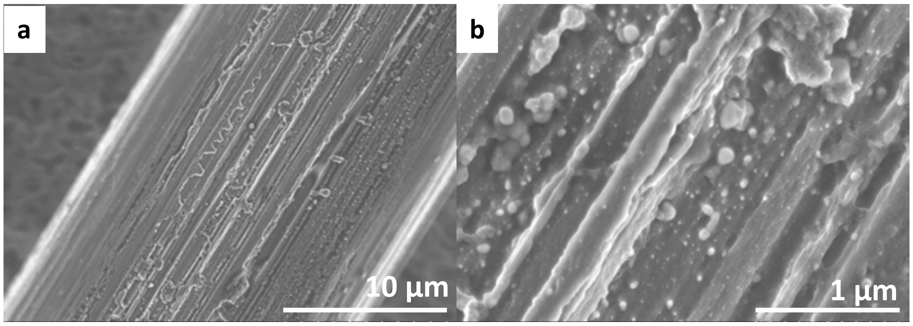


Figure 24. SEM images of the surface of C-C1 carbon fibers.

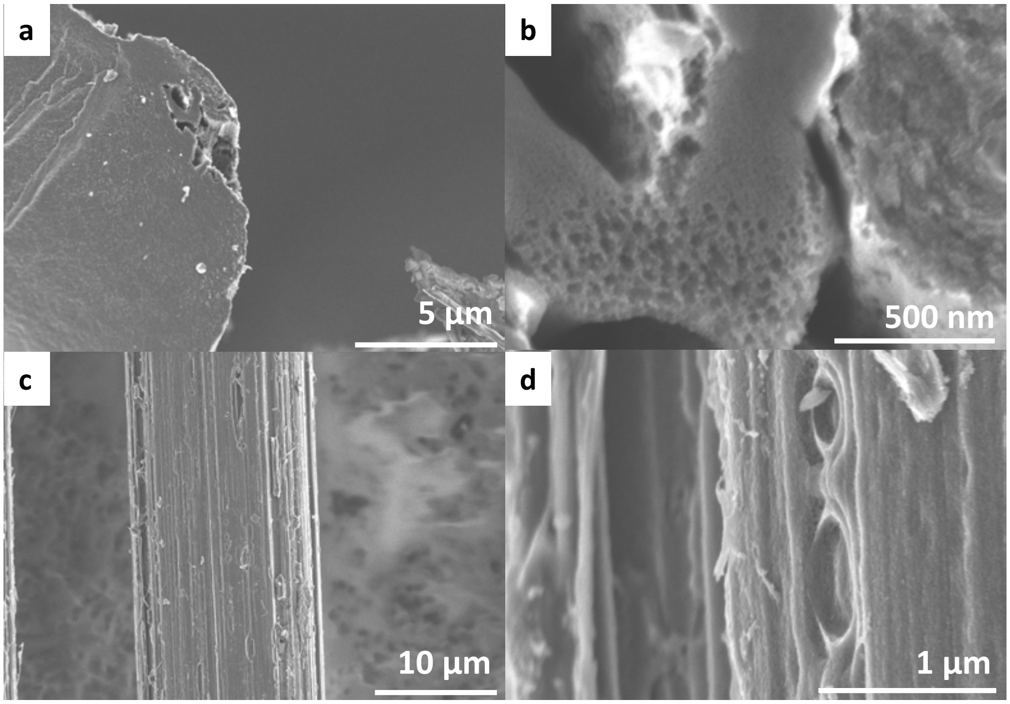


Figure 25. SEM images of the cross-sections (a-b) and surface (c-d) of C-C2 carbon fibers.

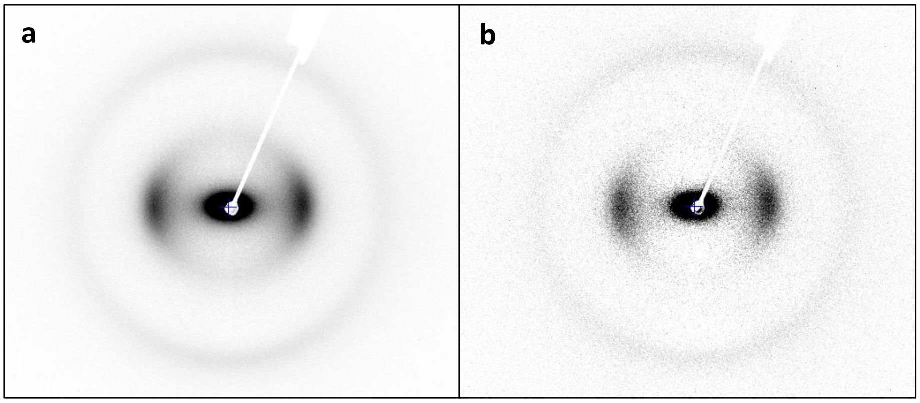


Figure 26. 2D WAXD patterns of carbon fibers. (a) C-C1 and (b) C-C2.

Table 6. Structural parameters of f-Asp/PAN based carbon fibers.

	B-C1 f-Asp/ PAN (30/ 70)	**B-C2** f-Asp/ PAN (30/ 70)	**C-C1** f-Asp/ PAN (60/ 40)	**C-C2** f-Asp/ PAN (60/ 40)
L002 (nm)[a]	1.45	1.34	1.43	1.56
L10 (nm)[b]	1.91	1.80	2.2	2.2
f_{002}[c]	0.73	*0.48-0.58	0.55	0.68

[a] *Crystal size of (002) plane at* $2\theta \sim 26°$, *according to Scherrer's equation with* $K = 0.9$.

[b] *Crystal size of (10) plane at* $2\theta \sim 43°$, *according to Scherrer's equation with* $K = 0.9$.

[c] *Orientation factor of (002) plane, calculated from the azimuthal scan (and adding the contribution after deconvolution of peaks around* $2\theta \sim 26°$ *from the meridional scans in the case of B-C2 and C-C1)*

* *Meridional scan of C-C1 fibers showed multiple peaks around* $2\theta \sim 26°$ *and hence the orientation factor is reported over a range (Figure 20c).*

4. Conclusion

As-received asphaltenes (S1; Asp), were not fully soluble in DMAc, DMF or DMSO. Functionalization of asphaltenes through nitric acid resulted in successful asphaltene dissolution in DMAc and further aided in the preparation of relatively homogenous blend solutions with PAN. Asphaltenes (f-Asp) functionalization was confirmed using FTIR. Three spinning trials were conducted from f-Asp/PAN blends. Based on these trials, carbon fiber tensile strength and modulus from the f-asp/PAN blends were in the range of 0.4 to 1.1 GPa, and tensile modulus was in the range of 57 to 181 GPa. This study opened up avenues to use asphaltenes as carbon fiber precursors through potentially scalable route of solution/gel spinning of functionalized asphaltenes while blending with polyacrylonitrile. Further balance between the blend ratio of functionalized asphaltene and PAN, using methanol functionalized asphaltenes, spinning bicomponent fibers with homogeneous solutions and optimizing stabilization/carbonization conditions, are some of the potential pathways to improve the properties of the asphaltene based carbon fibers, beyond what has been done in this study.

Appendix A. Solubility studies of Alberta Oil Asphaltenes (Asp)

Solubility of as-received asphaltene powder (Asp) in dimethylacetamide (DMAc), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and their solvent mixtures in either in toluene or acetone was studied. Based on its solubility parameters, asphaltene is expected to be soluble or partially soluble in solvents such as DMF and DMAc if the asphaltene Hildebrand solubility parameter is in the range of 20-24 $MPa^{0.5}$, which is largely dictated by the asphaltene source [[14]].

Dried Asp (2 g) was added to 10 mL of solvents or solvent mixtures as listed in Table A1, sonicated for 1 h, and then centrifuged at 10,000 rpm for 30 minutes. The supernatants were decanted, and the sediments were dried in vacuum at 90 °C for 48 hours. The sediment weights listed in Table A1 shows that 46% Asp was insoluble (54% soluble) in DMAc, while 99% Asp was insoluble in DMSO and DMF. Solubility further improved among solvent mixtures, and 39% Asp was insoluble in DMAc/toluene (60/40). DMF/acetone (60/40) dissolved only about 2% Asp.

Table A1. Dry sediment weights (in grams) after being centrifuged at 10,000 rpm in respective solvents and solvent mixtures. Initial Asp weight in each case was 2 g in 10 ml of solvent.

Solvent (v:v) ratios	**100:0**	**90:10**	**80:20**	**60:40**
DMF:Acetone	1.97	1.92	1.95	1.94
DMSO:Toluene	1.98	1.87	1.78	1.74
DMAc:Toluene	0.92	0.96	1.04	0.78

Attempts were made to make a spinnable slurry from PAN/Asp in DMAc, DMSO, as well as in DMAc/toluene and DMSO/toluene mixtures. However, these slurries were phase separated and not found suitable for fiber spinning (Figure A1 and A2). By comparison, PAN/f-Asp in DMAc formed homogeneous solutions/dispersions (Figure A3).

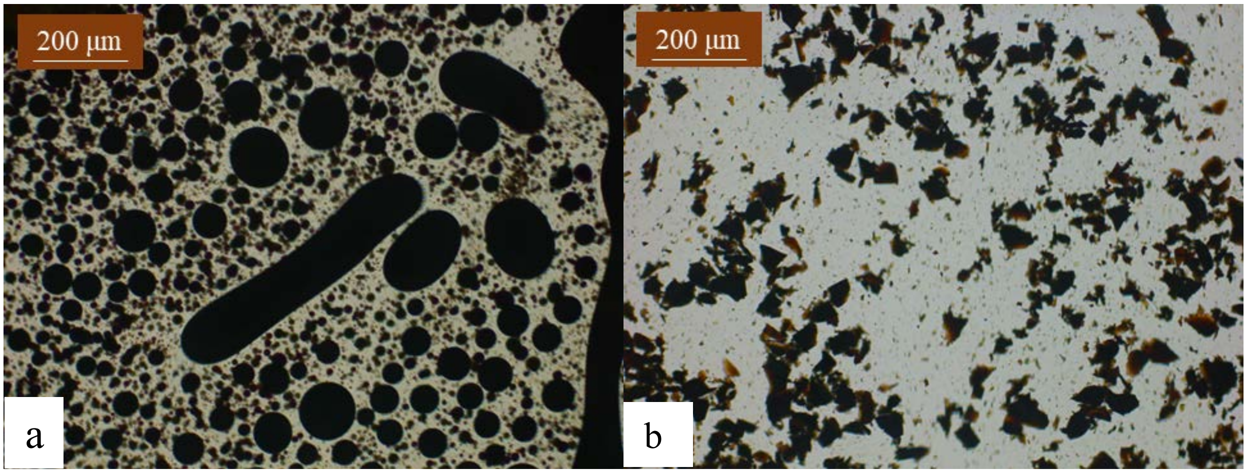


Figure A1. Optical micrographs of, a) 10 mL:10 mL of DMSO/toluene with 1.5 g PAN (Mv: 250, 000 g/mol) and 2.5 g Asp; b) 20 mL DMSO with 1.5 g PAN (Mv: 250, 000 g/mol) and 2.5 g Asp.

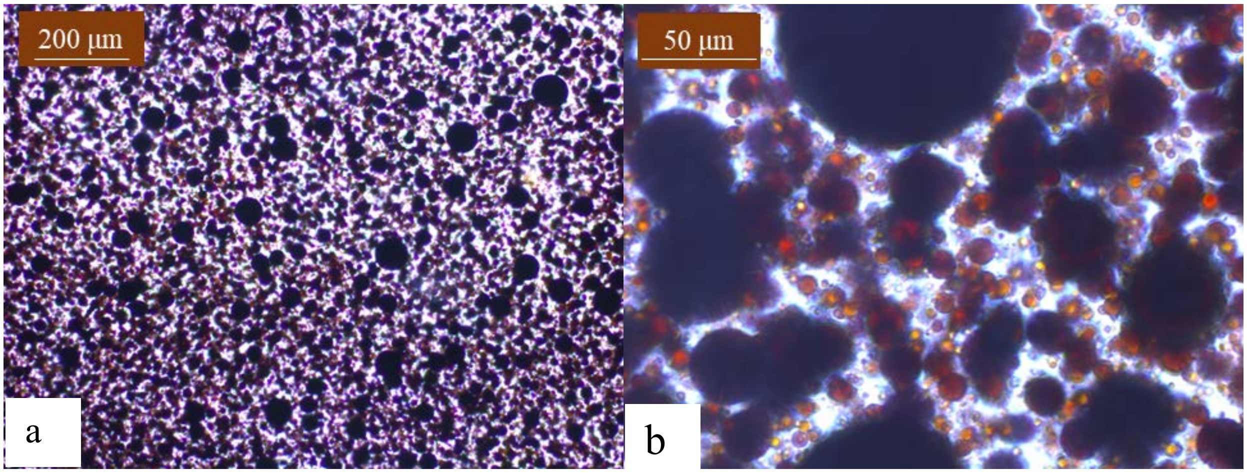


Figure A2. Optical micrographs: (a) 11 mL:9 mL of DMSO/toluene mixture with 1.75g PAN (Mv: 500, 000 g/mol) and 2.5 g Asp. (b) 20 mL DMAc with 1.15 g PAN (Mv: 500, 000 g/mol) and 1.75 g Asp.

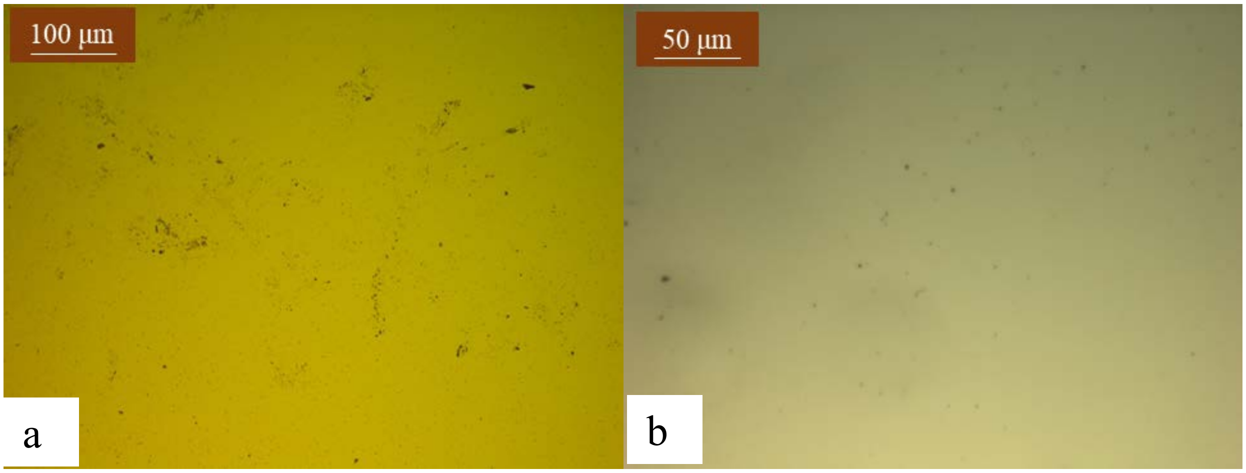


Figure A3. Optical micrographs of 20 ml DMAc with 1.15 g PAN (Mv: 500, 000 g/mol) and 1.75 g f-Asp.

Appendix B. Spinning of Alberta Oil Asphaltene (Asp) and Polystyrene (PS) blends

Spinning Trial 1

As-received asphaltene (Asp) powder was soluble in toluene, and the spinning of this solution was attempted but not successful. Thus polystyrene (PS) with a molecular weight of 350, 000 g/mol was added to the solution. Spinning solution was prepared by adding 6 g PS and 70 g Asp to 100 ml toluene in a 500 ml glass reactor. The suspension at room temperature was heated to 70 °C and stirred at 200 rpm for about 120 min. Fibers could not be pulled out using a glass rod from the solution at 70 °C. Hence, the temperature of the solution was decreased to 50 °C and fibers could be pulled out from the solution. At this stage, the solution was transferred to the solution barrel (spinning system), maintained at 50 °C. The solution was attempted to be extruded through a single hole spinneret (at a temperature of 60 °C) of 250 μm diameter. Rheological behavior of the solution was studied using an ARES Rheometer with parallel plate geometry (50 mm plate diameter and 1 mm gap between the plates) at room temperature. A constant strain of 1% was applied and the angular frequency varied from 0.1 to 300 rad/s. The viscosity of the solution measured at an angular frequency of 1 rad/s and room temperature over two trials were 5158 Pa.s and 4178 Pa.s. However, the attempt to spin the fibers was not successful as no jet of filaments was observed and the rotor of the spinning system stopped working. At this stage, the filter was removed from the spinning assembly and spinning was attempted through a 350 μm spinneret without filter. Continuous jet of filaments was achievable when the flow rate of the solution was set to the maximum limit of the system (at 2 cc/min). The next issue was the collection of continuous fiber. Extruding the jet in air did not work, as the flow rate of the extrudate was too high and there was not sufficient time for the solvent to evaporate. Initial extrusion of the jet into methanol or DMF did not result in coagulation. After about 30 min, the jet solidified in DMF or methanol, to clumped up brittle pieces (Figure B1).

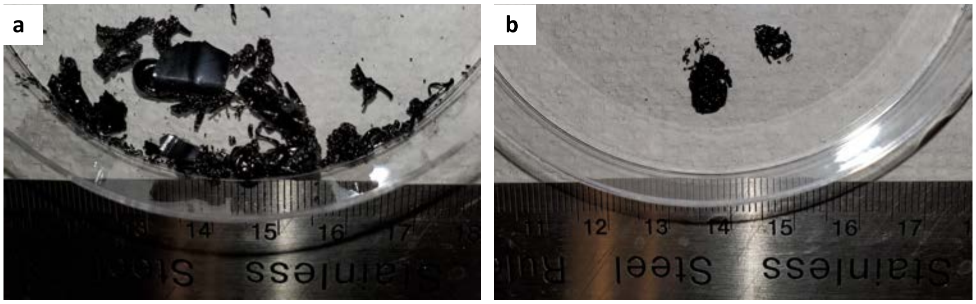


Figure B1. Jet from spinning trial 1 of Asp/PS blend solidified to brittle pieces in (a) DMF and (b) methanol.

Spinning Trial 2

With the single component spinning of Asp/PS blend being unsuccessful, an alternate method to spin the Asp solution was used by changing the geometry and addition of polyacrylonitrile (PAN; Mv: 250,000 g/mol). Bicomponent sheath-core geometry was attempted to spin the Asp with a reinforcing component of PAN. Asp/PS blend in toluene served as the core component while PAN in DMF was the sheath encapsulating the core. PAN was chosen to improve the spinnability of Asp-PS and resolve the issue of coagulation. With PAN now being situated in the sheath and Asp encapsulated, PAN would come in contact with the coagulation bath yielding fibers with structural integrity. The area ratio of sheath and core was controlled by adjusting the flow rates of the solutions. For this trial, extrusion was tried by maintaining the area of the sheath higher than that of the core (with the minimum area ratio of 64% sheath and 36% core).

The Asp/PS solution was prepared by following the same protocol, as elucidated in the spinning trial 1. For the PAN solution, 15 g of PAN was added to 100 ml of DMF, maintained in a pre-chilled ice bath (~ 0 °C) for 60 mins, to create a suspension. The suspension was then heated gradually to 70 °C and stirred at 200 rpm for 120 min. The viscosity of the Asp/PS solution at room temperature and 1 rad/s yielded widely varying values over two trials: 882 Pa.s and 46 Pa.s, while the viscosity of PAN solution was 46 Pa.s. Toluene evaporates when the Asp/PS solution is exposed to air and forms a film either during the loading of solution on the rheometer or during the viscosity measurement. This formation of film could possibly lead to the variation in the viscosity of the Asp/PS/toluene solutions.

The two solutions were transferred to the spinning barrels maintained at 50 °C and the extrusion was attempted through a 200 μm diameter spinneret maintained at 60 °C. Methanol at room temperature was used as the coagulation bath. When the two solutions were allowed to flow simultaneously, Asp/PS/toluene solution appeared to have coagulated the PAN/DMF upon contact in the spin pack, thus blocking the spinneret and resulting in no fiber extrusion. The next attempt was made using 350 µm spinneret and the PAN solution was allowed to flow first and then the Asp/PS solution, thus entrapping it within the PAN solution. This method prevented the coagulation of PAN and blockage of the spinneret. The spinneret temperature was maintained between 50-60 °C. During this attempt, filaments of PAN sheath with non-uniformly distributed Asp/PS was obtained (Figure B2). Continuous jet of filaments with Asp/PS uniformly encapsulated in PAN's sheath were not achieved in this trial. Hence the trial was suspended.

Figure B2. Filaments obtained from the spinning trial 2 with non-uniform distribution of Asp/PS (brown regions) in PAN (white/yellow regions).

Spinning Trial 3

The next system that was studied for their capability of spinning fibers with the aid of high-speed shear mixing (HSSM) (Equipment: DAC 150.1 from Flacktec Inc.) was the Asp-PS/toluene. Asp solution in toluene was prepared by adding 120 g of as-received Asp to 120 ml of toluene. The solution was stirred using magnetic bars at room temperature and then at higher temperatures by placing it on a hot plate with temperatures ranging from 50-75 °C, until a solution with no aggregates was obtained. PS solution was prepared in a glass reactor by initially adding 100 g of solids to 100 ml of toluene and heating to 70 °C using an oil bath. The suspension of PS in toluene was diluted to dissolve PS and form a solution with a final solid content of 69 g/dL. The PS solution was highly fiber forming and fibers of length >30 cm were easily pulled out from the solution using a glass rod. The two solutions namely, Asp in toluene and PS in toluene, were then mixed to make blends in the Asp/PS weight ratios of 60/40 and 80/20. The blends were mixed using two methods: (1) using a spatula or the low shear mix and 2) HSSM at 3000 rpm for two intervals of 5 min each. The microstructure of the four blends was observed through an optical microscope (Figures B3 and B4). From the micrographs of all the four blends, it can be seen that Asp and PS form phase separated structures. The effect of shear on mixing of these blends was evident through the micrographs. Upon increasing the speed of mixing, the size of the phase separated particles is found to be decreased and there seems to be more uniform distribution of the dispersed phase in the continuous matrix. Thus, high speed shear mixing is somewhat effective to obtain a uniform dispersion of these blends.

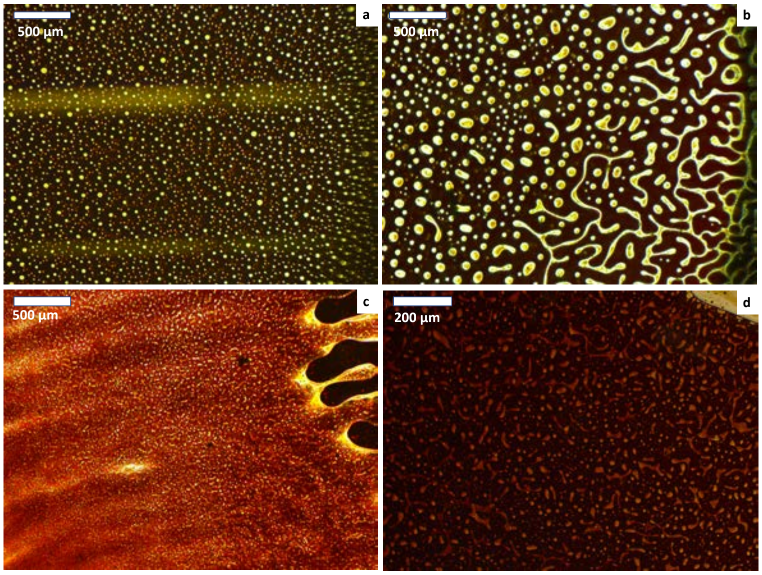


Figure B3. Optical micrographs of Asp/PS (80/20) solutions in toluene after low shear mixing (a-b) and high shear mixing (c-d). a and b, as well as c and d were imaged at two different locations of the respective dispersions.

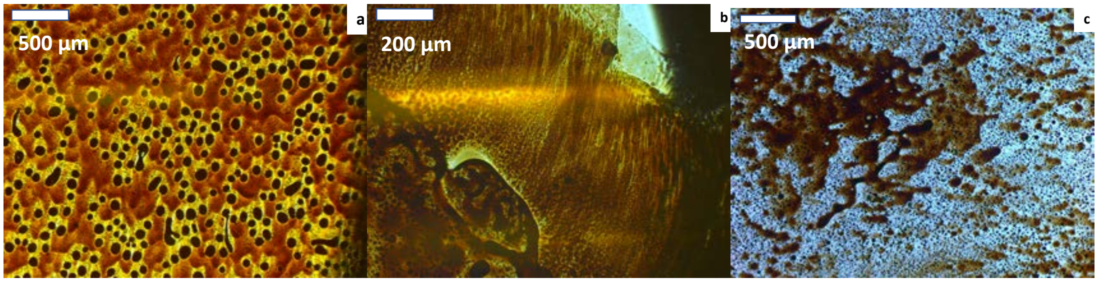


Figure B4. Optical micrographs of Asp/PS (60/40) solutions in toluene after low shear mixing (a-b) and high-speed shear mixing (c). a and b were imaged at two different locations of the dispersion.

The ease of formation of fibers from the HSSM blend solutions was tested by pulling out filaments from these solutions through a glass rod. Given the ease of fiber formability of the Asp/PS (60/40) system, compared to the Asp/PS (80/20), it was chosen as the system to attempt solution fiber spinning. Spinning solution (90 ml) was prepared by high shear mixing. The high shear mixing protocol used is elucidated as follows: two batches of Asp/PS solutions (45 ml each) in the weight ratio of 60/40 were each high shear mixed at 2500 rpm over two intervals of 5 min; the two batches were then combined into a single blend solution (90 ml) and then again mixed at 1500 rpm for the following time intervals: 2 min, 2 min, 1 min, 1min. The optical micrographs of the spinning solution after the high shear mixing protocol show Asp phase reasonably dispersed in PS (Figure B5). The viscosity of the solution measured at an angular frequency of 1 rad/s and room temperature over two trials were 1252 Pa.s and 875 Pa.s. Bradford system (Figure B6), with a solution barrel, piston, and spinneret, was used for spinning the blend solution through a 350 µm spinneret at room temperature. The flow rate was controlled by adjusting the speed of the piston. The fibers were extruded into air (dry spinning) and then wound onto plastic spools. Continuous jetting was observed in the range of piston speeds from 0.28 mm/min to 1.8 mm/min. However, at higher flow rates, the extruded fibers did not have sufficient time for the solvent to evaporate and coagulate into fibers to be collected on the spool. 0.28 -0.32 mm/min was the stable speed at which the fibers were extruded and collected on the spools. The draw ratio of the as-spun fibers is calculated as the speed of collection of the fibers at the spool divided by the speed of extruded fibers exiting the spinneret. Fibers were collected at draw ratios ~7, 10 and 27. The maximum draw ratio was found to be 51. But the most stable draw ratio for collection was ~7. The collected precursor fibers are categorized into three groups based on their draw ratios (Table B1).

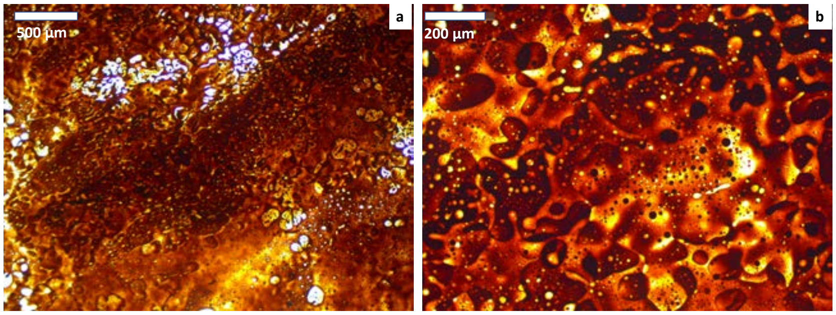


Figure B5. Optical micrographs of Asp/PS (60/40) spinning solutions in toluene after the high shear mixing imaged at magnifications of (a) 4x and (b) 10x.

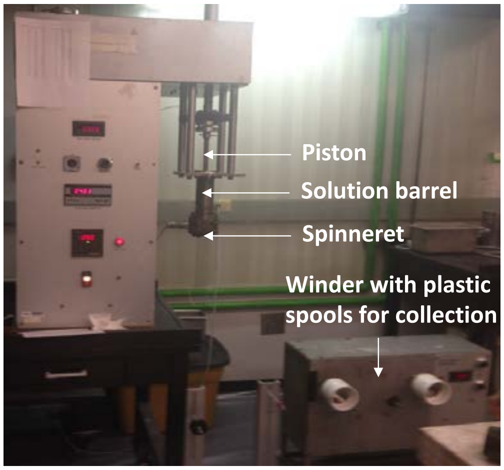


Figure B6. Photograph of the Bradford fiber spinning equipment.

Table B1. Details of the spools collected during spinning trial 3 of Asp/PS (60/40).

Spool Name	Ram Speed (mm/min)	Speed of winding (m/min)	Draw Ratio (DR)	Approximate length of collected fibers (m)
		Group 1		
T3S1	0.32	15	7.3	75
T3S2	0.32	15	7.3	45
T3S3	0.28	15	7.8	45
T3S4	0.28	15	7.8	150
T3S5	0.28	15	7.8	150
		Group 2		
T3S6	0.30	20	10.4	200
		Group 3		
T3S7	0.29	50	26.8	100

Figure B7 shows the extruded fibers collected on plastic spools. It was observed that often, more than one filament on the spool were fused together and separating the filaments led to their breakage. Given that these fibers had 40 wt% of PS, they were extremely brittle as expected and broke into smaller segments preventing their continuous unwinding.

Single filament tensile testing was performed using the RSA III Solids analyzer and at least 5 filaments were tested. The fibers were mounted paper tabs with half-inch gauge length, to be tested for the tensile properties. Mechanical properties of the fibers are listed in Table B2. During the mechanical test it was observed that the fibers broke near the grip, in most of the cases. The group 3 fibers with the highest draw ratio seem to have the best mechanical properties among the fibers produced in this trial.

Table B2. Mechanical properties of the precursor fibers of Asp/PS (60/40) blend.

	Group 1 (TDR ~7)	**Group 2 (TDR ~10)**	**Group 3 (TDR ~27)**
Diameter (μm)	82 ± 7	70 ± 7	46 ± 76
Tensile Strength (MPa)	7.1 ± 1.1	6.2 ± 3.2	11.5 ± 2.1
Tensile Modulus (MPa)	853 ± 110	1128 ± 243	1380 ± 314
Elongation at Break (%)	0.89 ± 0.16	0.54 ± 0.21	0.84 ± 0.21

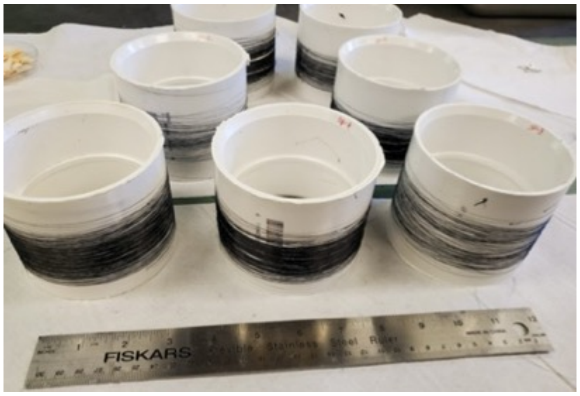


Figure B7. Representative precursor fiber spools of Asp/PS (60/40) obtained in Trial 3 spinning.

Group 1 precursor fibers (T3S3) were stabilized without the application of tension. Fibers were first soaked in spin finish solution (SF-LUROL CF-14676 supplied by Goulston Technologies, North Carolina; Concentration: 1.5 wt% of spin finish in deionized water) for 2h, heated at 3 °C/min to 350 °C and held for 170 min, then heated at 3 °C/min to 375 °C and held for 10 min. At the end of stabilization, the length of the fibers after stabilization decreased on an average by ~ 27%. The fibers were fused together, despite the application of spin finish. The fibers were brittle, and it was difficult to separate the fibers into single filaments as they broke while doing so. Figure B8 shows the experimental setup before and after stabilization. Based on fusion of the stabilized fibers, these fibers were not carbonized.

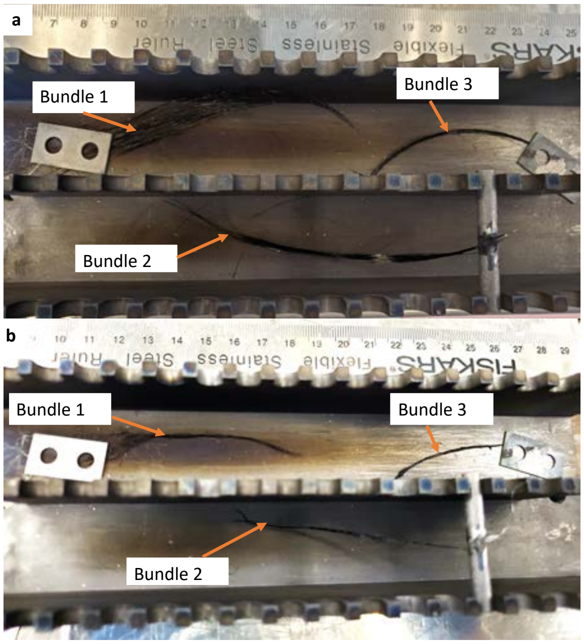


Figure B8. (a) Experimental set up for stabilizing Asp/PS (60/40) precursor fibers and (b) stabilized fibers.

Integrated WAXD scans of the as received asphaltene powder, precursor and stabilized fibers (Figure B9) were obtained using Rigaku MicroMax 002 X-ray generator (Cu Kα radiation, λ = 1.5418 Å, 50 kV and 0.6 mA) equipped with a R-axis IV++ detector. Asphaltene powder showed three peaks 2θ~11-20º, ~26º and ~43º, consistent with literature [27,28]. Polystyrene has amorphous peak around 2θ~20 º. The precursor fibers also showed all the three characteristic peaks of asphaltenes. Stabilized fibers showed an increase in the intensity of 2θ~26º peak relative to the 2θ ~11-20º peak, when compared with the precursor fibers.

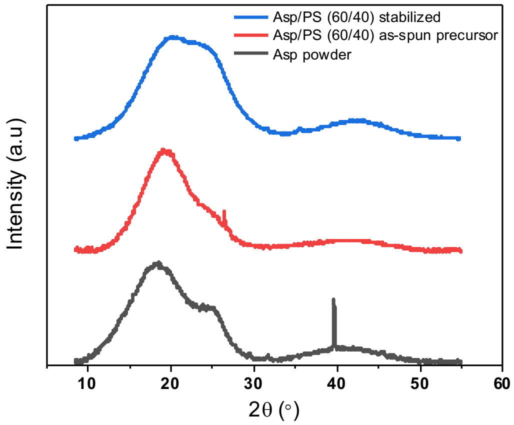


Figure B9. Integrated WAXD scans of Asp powder, Asp/PS (60/40) precursor and Asp/PS (60/40) stabilized fibers.

Summary

Spinning of asphaltene fibers by blending with PS was attempted. Spinning fibers with Asp/PS (PS less than 10 wt%) was not successful due to the issues with continuous jetting and coagulation. The next attempt involved spinning bicomponent fibers with Asp/PS/toluene in the core and PAN/DMF in the sheath. The trial yielded non-continuous filaments with Asp non-uniformly distributed in PAN. Also, the spinning had to be suspended due to the blockage of the spinneret by the coagulation of PAN upon contact with the Asp/PS/toluene solution.

Asp/PS blends with PS content of 20 and 40 wt% were then studied through low and high shear mixing. The high shear mixed Asp/PS (60/40) solutions were chosen as the spinning system due to their better fiber formability after the preliminary studies. Precursor fibers of Asp/PS (60/40) had tensile strength of 11.5 MPa and modulus of 1.4 GPa. Precursor fibers fused upon stabilization. Recommendations for future studies would be to modify the stabilization protocol to prevent fusing.

Appendix C. Melt compounding and extrusion of Asphaltene (Asp) and Polyacrylonitrile (PAN) blends

Melt compounding and extrusion of Asp/PAN blends were attempted. The effect of plasticization in these blends through the use of solvents, namely toluene for Asp and dimethylacetamide (DMAc) for PAN, was studied.

First the method of obtaining plasticized Asp and PAN using the solvents is described. 27 g of Asp was ground finely using mortar and pestle. Similarly, 15 g of PAN (Mv: 250,000 g/mol) was separately ground into a fine powder using mortar and pestle. Asp powder was transferred to the mortar, and 13 vol% of toluene was added slowly and mixed using the pestle. Asp/toluene (87/13) (vol%/vol%) mixture had some flakes due to the absorption (wetting) of the solvent onto the asphaltene. PAN/DMAc mixture was prepared in the same manner by addition of 20 vol% DMAc. PAN/DMAc (80/20) mixture had a granulated appearance, upon wetting of PAN by the solvent. The two mixtures were then sonicated separately for 1 h. After sonication, the flakes in the Asp/toluene (87/13) seemed to have decreased in size while no significant visual changes were observed for the PAN/DMAc (80/20).

Three trials of melt compounding and extrusion of the Asp/PAN blends from the plasticized samples described in the previous paragraph were conducted using the micro-compounder (DSM Xplore 15 cc). A spinneret of 500 μm diameter was used to extrude the filament into air and the filaments were attempted to be collected on plastic spools. The Asp/PAN weight ratio in all the trials was maintained at 60:40.

Trial A: Asp/toluene (87/13) and PAN/DMAc (80/20)

Asp/toluene (87/13) and PAN/DMAc (80/20) mixtures with the Asp/PAN weight ratio of 60:40, were blended together using the mortar and pestle (Figure C1). This blend weighing about 13.2 g in total was fed into the micro-compounder, with the initial compounding temperature set to 140 °C. The blend was mixed in the compounder for 10 min at 150 rpm and the force recorded during that time was ~2400 N. The blend was extruded at 10 rpm (Force: ~800 N) through the spinneret and collected on a winder at speeds ranging from 1.5 -2.5 m/min. The maximum speed of collection achieved was 3.8 m/min. The fibers obtained were rigid but could be successfully wound on the plastic spool. The compounding temperature was increased to 150 °C and the blend allowed to mix for 5 min. These fibers were again extruded at 10 rpm (Force: ~500 N) and collected on the spool with the winding speed around 1.2 m/min. The blend was further compounded at a temperature of 170 °C for 3 min and extruded at 10 rpm. The fibers could be obtained only at speeds below 1.1 m/min, for about 30 s.

Figure C1. Blend feed of Asp/toluene (87/13) and PAN/DMAc (80/20), used for Trial A.

Trial B: Asp/PAN (No plasticizers)

This trial of melt compounding and extrusion was conducted with just the Asp/PAN powders without plasticizer. About 7.2 g of Asp and 4.8 g of PAN powders were blended together in the mortar and pestle, as a feed to the micro-compounder (Figure C2). Based on Trial A, the initial temperature of compounding was set to 150 °C and the blend was attempted to be fed. At this temperature, without the plasticizers, the entire feed of 12 g could not be loaded into the micro-compounder. The compounding screws stopped working and the temperature was increased to 170 °C, in an attempt to soften the blend. The screws did not work at 170 °C either and hence, the temperature was momentarily raised to 200 °C, to initiate the movement of the screws. This attempt was successful and as the screws started moving at 2 rpm. The temperature was brought back to 170 °C and the entire feed was now loaded, albeit at lower speed of the screws (25 rpm vs 150 rpm), as the force experienced at 25 rpm was ~4500 N. The blend was compounded for 10 min and extruded at 10 rpm (Force: ~ 2700 N) onto the spool at speeds of 1-2 m/min. The temperature was then decreased to 150 °C and extrusion was attempted at 10 rpm (Force: ~2100 N). But continuous filaments could not be wound onto the plastic spools.

Figure C2. Blend feed of Asp and PAN powders used for Trial B.

Trial C: Asp/toluene (74/26) and PAN/DMAc (60/40)

From Trials A and B, it can be concluded that the addition of solvents as plasticizers to the Asp/PAN blend is beneficial. Hence, in this trial, the quantity of plasticizers was further increased, and the blends were compounded and extruded. Asp/toluene (74/26) and PAN/DMAc (60/40) mixtures were blended together in the mortar and pestle, to obtain the 13.2 g of feed for compounding (Figure

C3). The compounding temperature was set to 150 °C and the blend mixed for 10 min at 150 rpm (Force: ~2300 N). The blend was extruded at 10 rpm (Force: ~400 N) but uniform and long filaments were not obtained as the extruded material was still soft. The melt compounding temperature was thus decreased to 130 °C and mixed for 10 mins at 150 rpm (Force: ~2000 N). Upon extrusion at 10 rpm (Force: ~880 N), continuous filaments with non-uniform and rough surface were collected on the spools at speeds ranging from 1.5-2 m/min. The maximum speed of collection without any breakage was 2.9 m/min. The compounding temperature was further decreased to 115 °C to reduce the roughness on extruded filaments and improve their uniformity. The blend was compounded for 5 min at 100 rpm (Force: ~2400 N) and extruded at 10 rpm (Force: ~1590 N). The uniform filaments with smooth surface were collected on the spool at speeds ranging from 1.8 -2.2 m/min. The filaments were attempted to be extruded at 25 rpm, but they could not be collected on the plastic spool.

Figure C3. Blend feed of Asp/toluene (74/26) and PAN/DMAc (60/40) used for Trial C.

The force experienced by the blends both during the compounding and the extrusion, was lower than the force observed in Trials A and B under similar conditions. Thus, increasing the quantity of plasticizers further improved the processibility of these blends. Another significant change with the increase in quantity of the plasticizers is the reduction in the processing temperature from 170 °C to 130 °C and 115 °C. The list of the samples collected over the three trials (A, B, C) and the parameters (Table C1), as well as the images of the samples collected are presented (Figures C4-C6).

Table C1. Summary of the filaments collected over Trial A, B, C and the associated parameters.

Trial	**Sample Name**	**Processing Temperature (° C)**	**Force during compounding (N)***	**Force during start of extrusion (N)****
A	T4A1	140	2400	800
	T4A2	140	2400	800
	T4A3	150	-	500
	T4A4	170	-	-
B	T4B1	170	4500	2700
	T4B2	170	-	1900
	T4B3	150	-	2100
C	T4C1	150	2300	400
	T4C2	130	2000	880
	T4C3	130	2000	880
	T4C4	115	2400	1590
	T4C5	115	2400	1590

**Speed during compounding was 150 rpm except for these cases: T4B1, T4B2 (25 rpm) and T4B3 (10 rpm); T4C4 (100 rpm).*
***Speed during extrusion was 10 rpm except for this case: T4C5 (25 rpm).*

Figure C4. Representative fiber samples collected during (a)Trial A, (b) Trial B and (c) Trial C.

Summary

Plasticization of Asp and PAN, through the solvents was effectively achieved, as the processing temperature of the blends decreased with the increasing quantity of plasticizers in the blend. Without any plasticizers, filaments from Asp/PAN blend were successfully obtained at compounding temperature of 170 °C. On addition of 20 vol% of DMAc to PAN and 13 vol% of toluene to Asp, filaments were extruded and wound on the spool, at processing temperatures of 140, 150 and 170 °C. On doubling the quantity of plasticizers in the blend (40 vol% DMAc to PAN and 26 vol% of toluene to Asp), fibers with smooth surfaces were obtained and wound at compounding temperature of 115 °C. The force experienced by the three groups of blends, at a given temperature and speed of compounding or extrusion, decreased with the increasing quantity of plasticizers in them, as expected. Thus, the addition of plasticizers is an effective way to process the Asp/PAN blends at lower temperatures and with lesser force.

Appendix D. Spinning of Alberta Oil Asphaltene (Asp) and Polypropylene (PP) blends

Fibers from blend of Asp and PP (SABIC PP FPH50) were obtained through melt compounding and extrusion. All the Asp/PP blend fiber extrusions were done using a micro-compounder (DSM Xplore 15 cc). Asp and PP powders in the designated weight ratios were mixed and used as a feed for the compounding. A spinneret of 500 μm diameter was used to extrude the filament into air and the filaments were attempted to be collected on plastic spools. Figure D1 shows representative fibers collected on plastic spools. Table D1 summarizes the samples collected, the temperature used for melt compounding and the collection speed of fibers. The collection speed decreased with increasing asphaltene content.

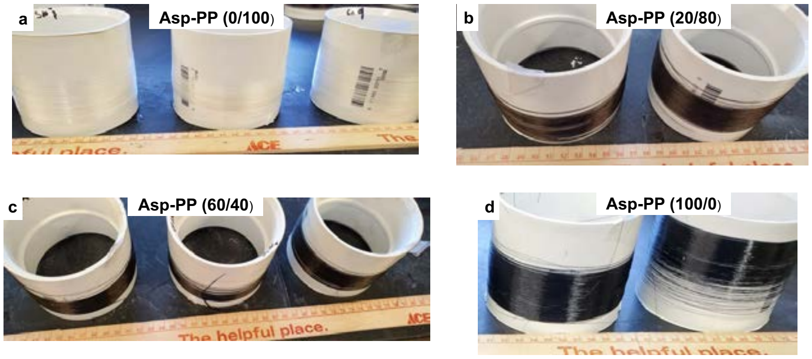


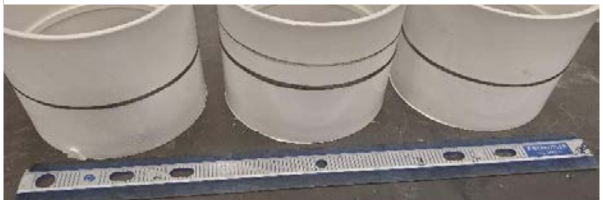
Figure D1. Representative as-spun fibers: (a) Asp/PP (0/100), (b) Asp/PP (20/80), (c) Asp/PP (60/40) and (d) Asp/PP (100/0).

Table D1. Summary of the Asp/PP blend fibers collected and the associated parameters.

Asp/PP (wt%/wt%)	Sample Name	Processing Temperature (°C)	Collection Speed (m/min)
Asp/PP (0/100)	T5A1	220	35-78
	T5A2-T5A3		78
Asp/PP (20/80)	T5B1	240	30-83
	T5B2		80
Asp/PP (40/60)	T5C1	240	20-67
	T5C2		56
Asp/PP (60/40)	T5D1	240	20-70
	T5D2		30-70
	T5D3		55
Asp/PP (80/20)	T5E1	240	30-67
	T5E2		55
	T5E3		40
	T5E4		29 (stable)
Asp/PP (100/0)	T5F1-T5F2	240	20-22
	T5F3-T5F4		14.7 (stable)

As-spun fibers of Asp/PP (20/80) and Asp/PP (60/40) were further drawn through a glycerol bath maintained at 130-135 °C (Drawn fibers shown in Figure D2). Hot draw ratio for both the fibers was 2. Asp/PP (100/0), without the PP, could not be hot drawn at this temperature. Table D2 lists the mechanical properties of the Asp/PP (20/80), Asp/PP (60/40) and Asp/PP (100/0) fibers. Fibers of Asp/PP (20/80) and Asp/PP (60/40) showed significantly large variation in diameter. Mechanical properties decreased with the increasing asphaltene content. Asp-PP (20/80) fibers produced in this study showed tensile modulus higher than control PP fibers (4.6 GPa) reported previously [[33]]. Thus, asphaltene could be potentially serve as a low-cost filler in PP fiber for certain applications.

a. Asp-PP (20/80)
As-spun speed of Collection: 80 m/min
HDR: 2



b. Asp-PP (60/40)
As-spun speed of Collection: 55 m/min
HDR: 2

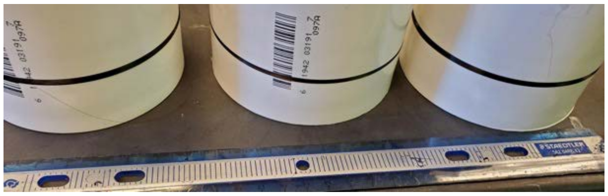


Figure D2. Representative drawn precursor fibers: (a) Asp-PP (20/80), and (b) Asp-PP (60/40).

Table D2. Mechanical properties of Asp-PP fibers.

	Asp/PP (20/80) **T5B2-2** **Drawn**	**Asp/PP (60/40)** **T5D3-5** **Drawn**	**Asp/PP (100/0)** **T5F3** **As-spun**
Diameter (μm)	36 ± 18	57 ± 27	62 ± 7
Tensile Strength (MPa)	235 ± 22	67 ± 14	11 ± 0.3
Tensile Modulus (GPa)	5.3 ± 0.8	2.7 ± 0.6	0.6 ± 0.4
Elongation at Break (%)	115 ± 49	37 ± 24	2.2 ± 0.6

Stabilization of fibers with asphaltene as the majority component (60 wt%) was attempted, without the application of any tension. Three bundles of drawn fibers of Asp/PP (60/40) were soaked in the spin finish solution (SF-LUROL CF-14676 supplied by Goulston Technologies, North Carolina; Concentration: 5 wt% of spin finish in deionized water) for 2h. The fibers were heated at 3 °C /min to 350 °C and held for 170 min, and then heated s at 3 °C /min to 375 °C and held for 10 min. At the end of stabilization, length of the fibers in Bundle 1 decreased by ~67 %. During this process, fibers fused together. Fibers were brittle and it was difficult to separate the fibers into single filaments as they broke while doing so. Fibers from Bundle 2 did not survive the stabilization process. While for Bundle 3, very few filaments that were stuck to the base of the holder were found. Figure D3 shows the fibers before and after stabilization.

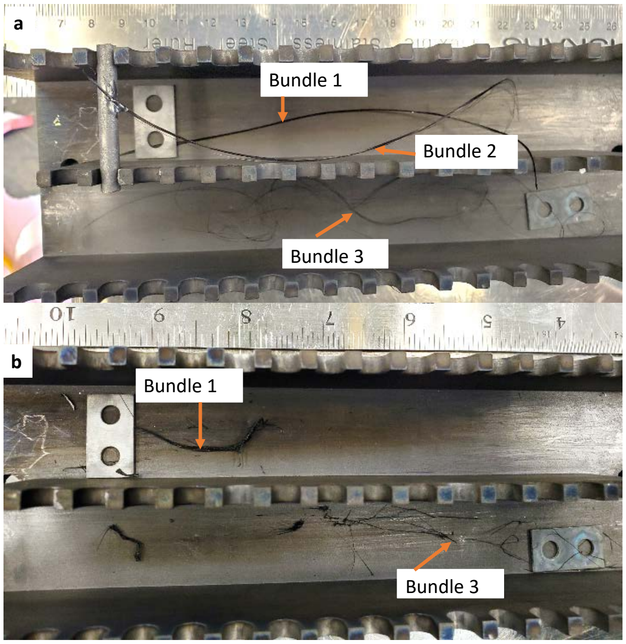


Figure D3. (a) Experimental set up for stabilizing Asp/PP (60/40) precursor fibers and (b) stabilized fibers.

Wide angle X-ray diffraction (WAXD) using CuK$_\alpha$ (λ = 0.1542 nm) manufactured by Rigaku Micromax-002 (operating voltage and current 50 KV and 0.60 mA) was conducted on Asp powder and Asp/PP (60/40) drawn precursor and stabilized fibers. Figure D4 shows the corresponding integrated WAXD scans. Asp powder had three characteristic peaks 2θ~11-20º , ~26º and ~43º, as reported in the literature [27]. Characteristic peaks of PP at 2θ~14º, 17º, 18.5º, 21º, 22º are dominant in the precursor fiber [34]. PP's characteristic peaks were still present in the stabilized fibers indicating that further work is needed to stabilize this fiber.

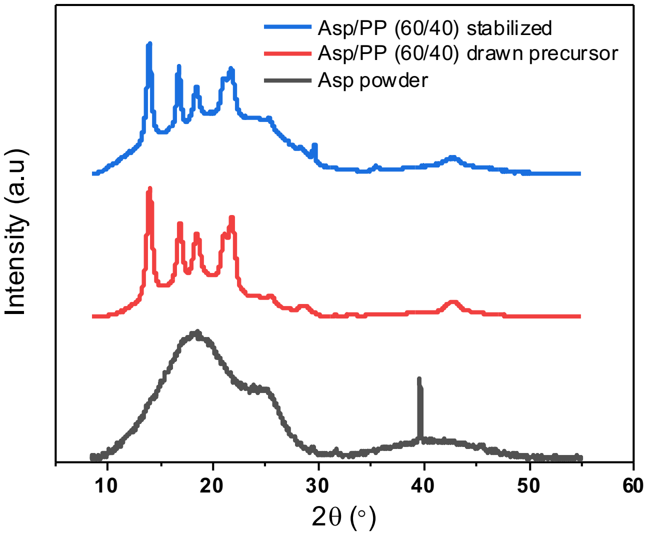


Figure D4. Integrated WAXD scans of Asp powder, Asp/PP (60/40) drawn precursor and Asp/PP (60/40) stabilized fibers.

Summary

Asp/PP fibers of various compositions (wt%/wt%) were melt compounded and extruded. Ductility of the fibers decreased with the increasing content of PP in the fibers. Fibers of Asp-PP (20/80) and Asp-PP (60/40) were successfully hot drawn. Fibers of Asp/PP (100/0) were brittle and hot drawing the fibers at 135 °C was not feasible. Asp/PP (20/80) drawn precursor fiber of tensile strength 235 MPa and tensile modulus 5.3GPa were made. PP and other thermoplastic composite fibers with Asp as filler could be of potential interest. Asp/PP (60/40) drawn precursor fiber of tensile strength 67 MPa and tensile modulus 2.7 GPa were made. Stabilization of these fibers was attempted, but not complete. Further recommendation for Asp/PP fibers would be to look into the prospect of Asp as filler for PP and other thermoplastic fibers. Asp/PP blend fibers can potentially be use for concrete reinforcement. As for manufacturing carbon fibers through this route, further work is needed to optimize the stabilization protocol before proceeding to carbonization.

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