

Preparation of Solid and Hollow Asphaltene Fibers by Single Step Electrospinning

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ABSTRACT

Electrospinning has been used to produce micrometer size fibers, both solid and hollow from non-covalently associating small molecules of a low grade hydrocarbon reject of crude oil, asphaltene. Asphaltene defined as a solubility class of crude oil is by no means a polymer but relatively large organic molecule of molecular weight ranging from 500 to 1000 Dalton. The production of asphaltene fibers is feasible by electrospinning because of its unique molecular structure which allows molecular aggregation. Fibers with diameter ranging from 2-20 μm were successfully spun from an asphaltene in toluene solution. Adding 2% hydrogen peroxide enhances electrospinning, leading to formation of hollow fibers, whereas adding 2% water inhibits electrospinning. The structure and morphology of the electrospun fibers were investigated with optical microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and time-of-flight secondary ion mass spectroscopy. The electrospun asphaltene fibers offer the potential for direct fabrication of membranes without use of multiple synthetic steps, complex electrospinning designs, or post processing surface treatments.

INTRODUCTION

Asphaltenes are components found in crude oil and bitumen. Defined as solubility class: insoluble in n-alkanes, such as n-pentane or n-heptane, and soluble in toluene. According to their chemical structure, they are aromatic multicyclic molecules surrounded and linked by aliphatic chains and heteroatoms. They are a mixture of large number of molecular species and hence are extremely complex and difficult to characterize. Their complex structure and polarity lead to their self association, flocculation and precipitation, depending on the properties of solvents. Due to these effects and their amphiphilic nature asphaltenes create problems in every stage of heavy oil processing such as clogging of wells, flowlines and surface facilities, and hence are considered undesirable components.^{1,2} Recently published molar mass data for crude oil asphaltenes ranges from 500 Dalton to 1000 Dalton.³

Electrospinning introduces electrostatic forces as the driving force to form ultra thin fibers. In this process, a polymer solution (in our case – asphaltenes) held by its surface tension at the end of a capillary tube is subjected to an electric field. With an increase in electric potential the charged pendent drop is deformed into a cone, known as ‘‘Taylor’s cone’’.⁴ At a critical field strength when the force due to the electric field overcomes the surface tension force holding the droplet, the solution starts to flow in the form of a charged jet. The jet moves towards the collecting counter electrode. While in transit, most of the solvent evaporates and the different polymer strands in the jet separate out due to mutual repulsion, a phenomenon known as ‘‘splaying’’. When these strands reach the collecting electrode their diameters are in the range of a few micrometers to nanometers. Continuous fibers are collected in the form of a nonwoven fabric.⁵⁻⁸

One of the suggested conditions necessary for electrospinning to occur is that the solution must consist of a polymer of sufficient molecular weight and minimum critical viscosity.⁹ As the jet of polymer solution leaves the tip of needle during electrospinning, it is stretched as it travels towards the collection plate. During the stretching of the polymer solution, it is the entanglement of the molecular chains that prevents the electrically driven jet from breaking up and thus maintaining a continuous jet. As a result, monomeric polymer solution does not form fibers when electrospun.^{9,10} Molecular weight of the polymer represents the length of the polymer chain, which in turn has an effect on the viscosity of the solution since the polymer molecular length is one of key properties determining the degree of entanglement of the polymer chains in a solvent. Hence, producing fibers of asphaltenes with a molecular weight in the range of 500-1000 Dalton would be considered infeasible unless there is some kind of network or entanglement between the individual molecules.

It is postulated that in aromatic solvents, asphaltenes are highly soluble, but above a certain concentration, known as the critical nanoaggregate concentration (CNAC) they can form nanoaggregates.¹¹ The CNAC data for asphaltenes in toluene have been determined using a variety of methods, such as laser thermal lensing,¹² fluorescence measurements,¹³ and high-quality-factor (high-Q) ultrasonic spectroscopy.¹⁴ Studies on Index-of-refraction show the importance of van der Waals interactions in controlling the solubility of asphaltenes in various types of solvents.¹⁵ It is well established now that the van der Waals attraction of aromatic rings balances with the steric repulsion of alkane chains, thereby determining the solubility of asphaltenes in various types of solvents.^{14,16} It is suggested by Andreatta, et al.¹⁴ that asphaltenes are shaped “like your hand” with aromatic rings being the palm and the alkane chains being the fingers. It is thought that the association of first few asphaltene molecules has fairly clear access to intermolecular interactions of the fused rings. The aromatic rings of different asphaltene molecules stack like “pancakes” to form nanoaggregates.¹⁴ However, subsequent aggregation of more molecules becomes constrained, due to the presence of alkane substituents, impeding further stacking. As a result of this steric repulsion, at some point, the interaction between a nanoaggregate and additional molecules becomes rather weak. At this point, new nanoaggregates form with increasing concentration but not an increase in the size of a single nanoaggregate.¹⁴ Finally, at very high asphaltene concentrations, the nanoaggregates undergo clustering with low binding energy between them.¹⁴ Here, we discuss electrospinning of these non-covalently associating small molecules. Through interactions such as hydrogen bonding, van der Waals forces, a sufficient number of clusters of nanoaggregates is reached that allows asphaltenes to electrospin successfully. The only other small molecules that have been used in electrospinning are phospholipids and very recently peptides.^{17,18} With careful variation and adjustment of the experimental parameters, we demonstrate the production of asphaltene solid and hollow fibers by electrospinning with diameter ranging from 2-20 μm . Our study shows that molecular weight is not a major criterion for electrospinning, rather the intermolecular forces between the asphaltene aggregates and hence molecular association are sufficient to mimic the chain entanglements observed in polymer solutions. Similar conclusions were reached by McKee, et al.¹⁷ while spinning phospholipids.

MATERIALS AND METHODS

Vacuum distillation bitumen feed contains ca. 0.5 wt% solids which consist of fine clays, mineral matters and solid hydrocarbons which are insoluble in toluene. The solids were removed by centrifugation of toluene-diluted bitumen at a toluene to bitumen volumetric ratio of 5:1 for 30

min at 20,000 rpm. The toluene was then removed from the bitumen solution by natural evaporation. Heptane was mixed with the prepared bitumen at a volume ratio of 40:1 to extract the asphaltenes. The *n*-heptane and bitumen mixture was shaken for 2 hours on a laboratory shaker and left overnight for asphaltene precipitation. The supernatant was then decanted and the asphaltene precipitates were repeatedly washed with *n*-heptane in a bottle until the supernatant became colorless. The solid asphaltenes were left overnight in a fume hood to evaporate the solvent. The asphaltene prepared as such is referred to as whole asphaltene. The mass of the whole asphaltene is about 11% of the original bitumen. Solutions with 10%, 15%, 20%, 30% and 40% (wt/wt) of asphaltene were prepared in toluene. The solutions were freshly prepared by adding a required amount of asphaltene into toluene under stirring at 20,000 rpm for 30 minutes. The resultant solution was sonicated for 30 minutes before electrospinning. In this study, silicon wafer was used as collector. The silicon wafer was made hydrophilic by thorough cleaning in a solution of hydrogen peroxide and sulphuric acid for about 30 minutes.

EXPERIMENTAL SETUP

The experimental setup is shown in *Figure 1*. A 3 ml syringe was connected through the needle to the one end of a Teflon tube with an internal diameter of 0.7 mm, and a stainless steel needle of the same diameter as the the one on the syringe was connected to the other end of the tube. The substrate was mounted to an adjustable laboratory screw jack. The stainless steel needle was connected to the positive terminal and the substrate to the negative terminal of a high voltage power supplier. During the experiment, a pendent drop of asphaltene in toluene solution was formed at the tip of the needle just before the application of electric potential. The applied voltage was gradually increased. With increasing applied potential the pendent drop elongated to form a Taylor cone at a critical voltage (~ 8 kV), at which a jet started from the tip of the cone. No good fibers were formed if electrospinning was performed at this critical voltage. In fact, there were more droplets rather than fibers deposited on the substrate collector. Therefore the voltage of electrospin was increased further to obtain better fibers.

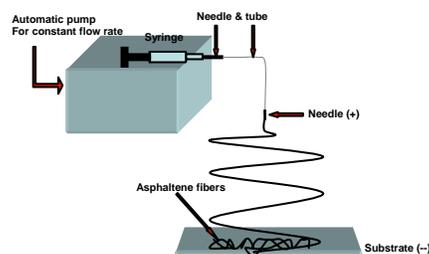


FIGURE 1. Experimental setup.

RESULTS AND DISCUSSIONS

We have previously described the importance of chain entanglements for the formation of electrospun fibers. Electrospun fiber formation would not be possible if the asphaltenes did not aggregate and form clusters of aggregates in some form of entangled network, as individual asphaltene molecules are low molecular weight compounds and hence incapable of forming entanglements. Another way to facilitate aggregation and result in greater clustering of aggregates within the solution is to increase the asphaltene concentration, which is similar to increasing molecular weight of a polymer. Thus asphaltene concentration was chosen as a variable while other electrospun conditions were fixed at 50 kV/m electric field strength, 1 $\mu\text{L}/\text{min}$ syringe flow rate, and 30 cm working distance. Such preferred conditions were arrived at by trial and error.

Optical microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) were used for characterizing the fibers. Before taking electron micrographs, the electrospun fibers were observed by optical microscope to confirm the formation of fibers. The SEM micrographs were obtained using Hitachi S-2700 Scanning Electron Microscope, after sputtering a carbon film of thickness around 5 nm on the substrate. 2 shows SEM micrographs of electrospun fibers that were formed from various concentrations of asphaltenes in toluene. At 20 wt% of asphaltenes in toluene, droplets were formed because of insufficient concentration, or in other words, limited clustering of asphaltene aggregates to form sufficiently entangled network, which resulted in the breakage of the electrified jet *Figure 2A*. All the formed droplets tend to collapse inward suggesting that they are hollow (shown by arrow). When the concentration was increased to 30% *Figure 2B*, fibers were formed, many of them with beads. During the evaporation of solvents from the fiber, Li et al.¹⁹ suggested that if the evaporation rate through the fiber surface is lower than the diffusion rate outwards the fiber, ballooning of the fiber is unavoidable; otherwise, no ballooning would occur and only dense fibers be obtained. For polymer solutions, reported studies indicated the requirement of a minimum critical viscosity to yield fibers without beads.^{9,10,20} When the viscosity is low, equivalent to low asphaltene concentrations in our case, it is common to find beads along the fibers deposited on the collection plate.

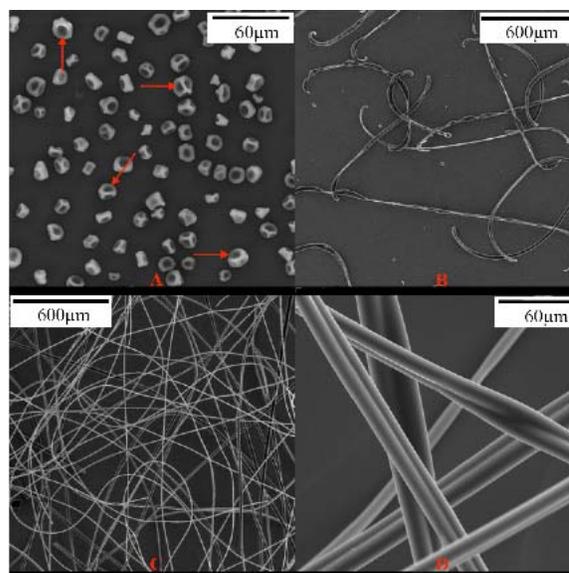


FIGURE 2. A is 20 wt% asphaltene in toluene. The surface of the droplets tends to collapse inward suggesting that they are all hollow (shown by arrow). B shows morphology of fibers formed from 30 wt% asphaltene in toluene solutions. C and D show morphologies of ribbon like fibers formed from 40 wt% asphaltene solutions.

A 35 wt% asphaltene concentration was still not sufficient for the formation of smooth fibers. However, at 40 wt%, uniform beadless fibers with an average diameter of 16 μm were formed and they were ribbon shaped *Figure 2C*. The fibers are shown at a higher resolution in *Figure 2D*. One possible mechanism for the formation of fibers might be the accumulation of asphaltene aggregates at interfaces. When the electrically charged jet is initiated and is on its path towards the collection plate, toluene evaporates from the surface of the jet, thereby increasing asphaltene concentration at the jet surface leading to further asphaltene aggregation at the air-toluene interface. As a result, the asphaltene aggregates form a skin on the liquid jet. Koombhongse et al.²¹ suggested that as the solvent diffuses out and evaporates, the atmospheric pressure tends to collapse the tube formed by the skin. The circular cross section, during the course of the collapse, initially becomes elliptical and then into ribbon-like shape with small tubes formed at each edge of the ribbon. This phenomenon was observed while spinning 10% poly(ether imide) in hexafluoro-2-propanol.

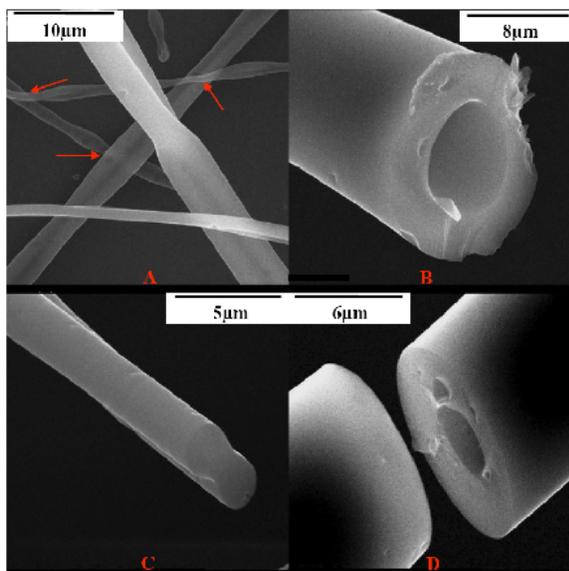


FIGURE 3. A and B are hollow fibers formed by the addition of hydrogen peroxide. The arrow marks in A indicate areas where we can clearly see that the fibers are translucent; C and D are formed by addition of water. Fiber in C is ribbon shaped and in D it is hollow with thick walls.

Hydrogen peroxide is a well known oxidizing and a cross-linking agent used in polymerization reactions. It was speculated that addition of hydrogen peroxide to an asphaltene solution could improve the fiber morphology. A 2 wt% hydrogen peroxide (with 30% strength) was added to a 20 wt% asphaltene solution. Hollow fibers *Figure 3A and 3B* were formed instead of ribbon-like shape as shown in *Figure 2*. The arrow markings in *Figure 3A* indicate areas where we can clearly note that the fibers are translucent. *Figure 3B* is an image of a hollow fiber. Hollow fibers are generally produced using methods such as direct co-axial electrospinning, chemical vapour deposition or by using special precursors. With these methods, annealing, sintering, calcination, etc. are often needed to achieve desired shapes.²²⁻²⁴ Our method, however, only uses a single step electrospinning to produce hollow fibers of asphaltenes. To illustrate the role of hydrogen peroxide, the same experiment was conducted with the addition of 2 wt% deionised water. The water formed a water-in-oil emulsion with an average water droplet size of 4 μm. When the mixture was electrospun, the fibers are a mixture of hollow and ribbon morphology *Figure 3C and 3D*. Decreasing the average size of the droplets to 2 μm inhibited fiber formation during electrospinning. This observation is attributed to aggregation or accumulation of asphaltenes at the water-oil interface rather than air-oil interface. In this case, as the surface area of the droplets increases with

decreasing size of the water droplets, insufficient asphaltenes are available at the air-oil interface, thereby limiting the formation of the asphaltene skin on the liquid jet and hence formation of asphaltene fibers. *Figure 4A and 4B* show a brittle fiber and a fiber that is broken into a large number of pieces. These fibers are formed while spinning 30 wt% asphaltene in toluene. The brittle nature of fibers suggest that the asphaltene fibers formed by electrospinning might be in the crystalline form. *Figure 4C* shows a wafer or foil of asphaltene formed while electrospinning 30 wt% asphaltene in toluene. *Figure 4D* shows the layered asphaltene skin on the surface of the fiber.

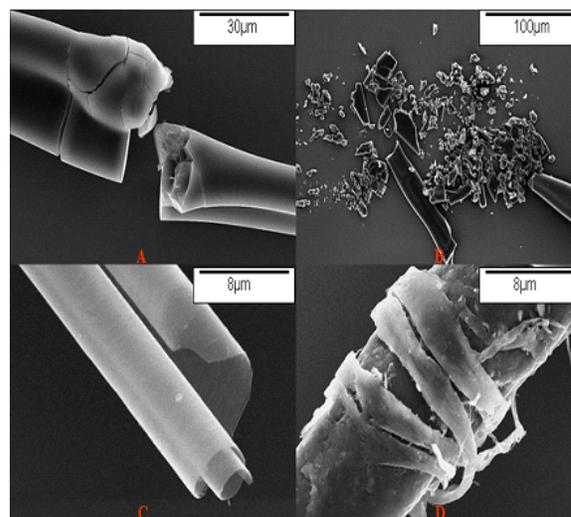


FIGURE 4. Different shapes of fibers formed during electrospinning of asphaltene. A and B show the evidence of fibers turning brittle after electrospinning. These fibers are formed by electrospinning 30 wt% asphaltene in toluene. C is a wafer or foil formed during electrospinning 30 wt% asphaltene in toluene. D shows the layers of asphaltene skin formation while spinning 20 wt% asphaltene with hydrogen peroxide in toluene.

FTIR spectroscopy was used to characterize asphaltene solutions before and after electrospinning. The concentration of asphaltenes in each sample was maintained at 30 wt% and corresponding FTIR spectra are shown in *Figure 5*. For the bulk asphaltene sample, the bands at 738, 849 and 894 cm^{-1} are attributed to aromatic C-H bending. Bands at 1378 and 1464 cm^{-1} are assigned to aliphatic C-H bending, and the band over 2700-2930 cm^{-1} represents aliphatic C-H stretching. Similar band assignments are reported for bulk asphaltene samples.²⁵ For samples after electrospinning, there are slight indications of new bands at 2270 cm^{-1} and 2580 cm^{-1} . They are attributed to R-N=C=O (isocyanates) and S-H stretching vibrations, respectively. We suspect that

the high electric field employed during electrospinning changed the conformation of some of these bonds, which has been reported in literature for other systems.²⁶ The nature of these changes needs to be studied further.

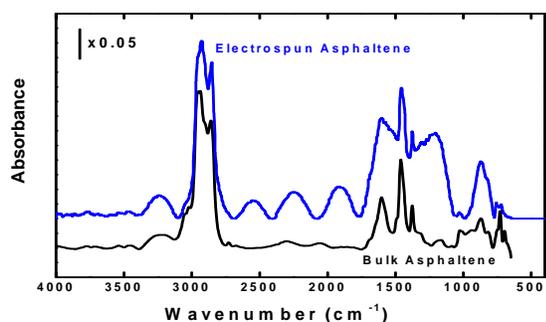


FIGURE 5. FTIR analysis of bulk asphaltene (blue lines) and electrospun asphaltene fibers (Red lines).

Figure 6 shows ToF-SIMS results for 35 wt% asphaltene samples. During electrospinning, samples for ToF-SIMS analysis were selected from the top, bottom, right, left and center of the substrate, to identify any pattern in the variation of the elemental compositions after electrospinning. The images in Figure 6 show that the fibers are mainly consisted of carbon and hydrogen with small amount of oxygen, sulfur and marginal amount of nitrogen, as anticipated. It was also found that the carbon to sulphur ratio in the fibers varied when moving from the edges of the collector towards the center. This observation indicates chemical alterations of asphaltenes after electrospinning. Systematic study is needed to investigate changes in structure and stacking sequence of asphaltene aggregates after electrospinning.

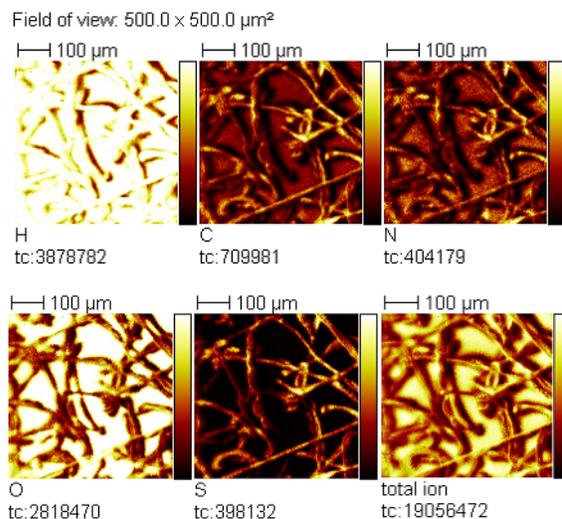


FIGURE 6. ToF-SIMS results for 35% asphaltene fibers. The image shows the elemental composition on the fibers. The bright colour indicates abundance of the substance and the dark colour signifies scarcity. Here H, C, N, O, S mean hydrogen, carbon, nitrogen, oxygen and sulphur. Also, tc is the total intensity of the individual element. The substrate here is silicon wafer.

CONCLUSION

This study shows that the intermolecular forces between asphaltene molecules are sufficient to form smooth fibers by electrospinning. Asphaltene fibers with an average diameter of 16 µm were successfully electrospun. Hollow fibers were observed when 2 wt% hydrogen peroxide was added to the asphaltene solution. Adding 2 wt% of water was found to inhibit electrospinning. There is indication that the high electric field employed during electrospinning caused chemical alterations of asphaltenes in the formed fibers.

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