Spring 2015

Electrospinning of S-B-S Triblock and S-I-S Triblock Copolymers For Use in Fuel Filtration

Kevin Houser
kph9@zips.uakron.edu

Electrospinning of S-B-S Triblock and S-I-S Triblock Copolymers For Use in Fuel Filtration

Kevin Houser

Department of Chemical Engineering

Honors Research Project

Submitted to

The Honors College

Approved:	Accepted:
George M Chase Date 13APR15	Date 13 APR '15
Honors Project Sponsor (signed)	Department Head (signed)
GEORGE G CHASE	H. MICHAEL CHEUNG
Honors Project Sponsor (printed)	Department Head (printed)
Bi-min Zhang Newby Date 4/13/2015	Date 13 APR '15
Reader (signed)	Honors Faculty Advisor (signed)
Bi-min Zhang Newby	H. MICHAEL CHEUNG
Reader (printed)	Honors Faculty Advisor (printed)
Date 4/13/2015	Date
Reader (signed)	Dean, Honors College
Gang Deng	
Reader (printed)	

Electrospinning of S-B-S Triblock and S-I-S Triblock Copolymers For Use in Fuel Filtration

Kevin Houser
The University of Akron

Abstract

The following research project looked into the potential of using nanofibers of syrene-isoprene-styrene triblock copolymer produced through the electrospinning process for the filtration of water out of fuel as well as a comparison of styrene-isoprene-styrene triblock to the styrene-butadiene-styrene triblock nanofibers produced at equivalent operating parameters. Based on the work completed, it is concluded that the styrene-isoprene-styrene triblock is not suitable for use in filtration with the current electrospinning conditions. On average, the styrene-isoprene-styrene triblock produced nanofibers of lower average diameter and lower standard deviation in diameter when compared to styene-butadiene-styrene triblock.

Executive Summary

Gasoline and diesel are the most widely used fuels used in automobiles in the world. The systems in place in our vehicles are sensitive and prone to damage under long term exposure to gasoline/diesel contaminated with water. Current purification techniques include absorption, coalescence, and stripping. Conventional filters absorb water by applying a media that has a high affinity for water and a low affinity for fuel. These filters eventually swell from the absorption of water and block flow. This paper will examine the possibility of using nanofibers spun from styrene-isoprene-styrene triblock copolymer to filter water from gasoline by its inherent hydrophobicity. The criteria for which hydrophobicity of the SIS nanofiber sheets will be judged is the water droplet contact angle. Superhydrophobic materials exhibit a water contact angle of >150°. The water droplet contact angle will be determined through the use of a goniometer. SIS nanofibers will be electrospun under multiple operating conditions to produce an array of nanofiber dimensions. A comparison study of SIS triblock copolymer and styrene-butadiene-isoprene will be presented to examine how the substitution of the isoprene repeat unit for the butadiene repeat unit in the polymer chain affects electrospinning characteristics and nanofiber properties. Nanofiber dimensions are determined by the use of scanning electron microscopy.

After images were taken of the SBS and SIS nanofibers the average and median nanofiber diameter as well as the standard deviation of the nanofibers were obtained from the images captured. Multiple images were captured and analyzed to ensure the data was not skewed by sampling only one portion of the nanofiber sheet. In general, the nanofibers produced using SIS were smaller in average diameter and deviated less from the average than those produced using SBS. SIS nanofibers ranged from 0.867 μm in diameter to 2.107 μm in diameter, while SBS

nanofibers ranged from 1.967 µm in diameter to 3.701 µm in diameter. SBS polymer solutions were able to be electrospun using lower polymer concentrations compared to SIS. SBS solutions were prepared at 11 and 12 weight percent SBS, while SIS solutions must have been prepared at higher concentrations of 14 and 15 weight percent SIS. SIS solutions of 10wt% to 12wt% produced microscale particulates instead of nanofibers.

In comparison of the water droplet contact angles of SIS nanofibers and particulates, the particulates on average achieved a higher contact angle. For the nanofibers, a peak water contact angle was observed around the 1 µm average fiber diameter, at which point the contact angle decreased with increasing and decreasing nanofiber diameters. Some error may be present in the measurement of the contact angle and the electrospinning conditions. The humidity and temperature of the lab in which the electrospinning experiments were performed were not measured and may have varied between experiments. The nanofiber sheets formed on the glass slides may have been collected unevenly or the thickness of the film collected on the glass slide from sample to sample may have been smaller or larger, thus affecting the water droplet contact angle.

At this point, a conclusion as to whether or not to use the SIS triblock copolymer for use in the filtration of water out of fuels is unable to be reached. It is recommended to continue research into the electrospinning of SIS triblock copolymers at varying styrene content to determine the effect of styrene content on the electrospinning process and nanofiber properties. It is also recommended to research other elastomeric copolymers to find a balance between monomer properties that will allow for adequate filtration properties.

Introduction

Gasoline and diesel are the most widely used fuels used in automobiles in the world. The systems currently in place in our vehicles are sensitive and are prone to damage under long term exposure to gasoline/diesel contaminated with water. When fuel is contaminated with water, "microbial growth and biodegradation of diesel fuel can cause filter plugging and more serious damages within the engine's fuel system" [1]. Other problems that may arise are holes in the fuel tanks and fuel injector failures [1]. Therefore, it is important to ensure that the fuels produced from the crude oil are as pure as possible throughout the transportation from refinery to engine. In order to achieve a high purity product, several methods are used to remove the water content from the fuel. These methods include absorption, coalescence, and stripping. Conventional filters absorb the water by applying a media that has a high affinity for water and a low affinity for fuel. However, these filters will swell from the absorption of the water, eventually blocking flow. It is proposed to use nanofibers electrospun from synthetic polymers into sheets to create filters that allow passage of the oligomeric fuels while blocking the water molecules.

This project researched the electrospinning of styrene-isoprene copolymers for use in the filtration of water from fuel streams. Previous work by Xu Zhang of the University of Akron has previously researched several polymers and copolymers and their electrospinning behaviors, but the styrene-isoprene-styrene triblock copolymer has yet to be characterized for its potential use in filtration. Comparisons to the previously researched styrene-butadiene-styrene triblock copolymer have been drawn based on nanofiber dimensions under similar electrospinning conditions. The electrospinning conditions' effect on nanofiber dimensions as well as the nanofiber dimensions' effect on the hydrophobicity of the fibrous sheets have been analyzed through this research.

Background

Electrospinning is a relatively simple process to produce submicron fibers from polymer solutions and polymer blends. Nanofibers produced from electrospinning have found focus in diverse applications, such as texturing, fiber reinforcement, tissue engineering, filtration, and sensing [2]. The process has attracted numerous attention since the 1990s for being the "the simplest approach to fabricate 1D nanostructures with both solid and hollow interiors with continuous length, tunable diameter, aligned direction, and diverse and controllable composition" [2]. In particular, the electrospinning of copolymers offers property enhancement of polymeric materials, "including tailoring of thermal stability, mechanical strength and barrier properties, and has therefore been often pursued for engineering structural applications" [3].

Multiple parameters affect the electrospinning process for polymer solutions, including concentration of the polymer solution, the molecular weight of the polymer, the applied voltage, the flow rate of the polymer solution through the needle tip, the distance from the needle tip to the collector, and the solvent(s) used in the polymer solution [3]. These parameters may be manipulated to form nanofibers of varying diameter and uniformity. Other parameters lie outside of control except in finely controlled labs, such as temperature and atmospheric humidity [3].

Previous work by Shuqin Feng and Xinyuan Shen has examined the electrospinning of styrene-isoprene-styrene copolymers and polystyrene. In their work, they manipulated solvent ratios of tetrahydrofuran and n,n-dimethylformamide along with polymer concentrations in the polymer solution. Feng and Shen concluded that with increasing DMF solvent fractions and increasing polymer concentration, the nanofiber diameters became homogenous and the beads on the fibers decreased. The presence of DMF resulted in a beneficial effect on fiber formation and increased

electrospinnability of SIS solutions [4]. Previous work by Feng et al. concluded the addition of DMF increased the electrospinnability of SIS fibers although the block copolymer could be dissolved in pure THF. They also found the range for electrospinnability for SIS to be between 8-15 wt% and the fiber average diameters to range from 100 nm to 1200 nm [5].

It is intended to use these nanofibers for the filtration of water out of organic fuels. Since the oligomeric fuels contain molecules much larger than water, the filter will not be able to filter out water by size exclusion. Therefore, it is intended to construct a nanofiber filter that repels water through its inherent hydrophobic properties. According to Lin Feng et al., super hydrophobic surfaces are surfaces in which water droplets form a contact angle of >150°. These surfaces have been produced mainly in two ways: creating a rough structure on a hydrophobic surface (CA>90°) and modification of a rough surface by materials with low surface free energy. The water contact angle has been used as a criterion for the evaluation of hydrophobicity of a solid surface [6]. Drop shape analysis has been widely adopted as a method to determine the contact angle of water droplets, and many new methods have been developed thanks to the age of digital computers, such as axisymmetric drop shape analysis (ADSA) and theoretical image fitting analysis (TIFA) [7]. Through the use of computer software, the contact angle of water droplets on nanofiber sheets may be determined, and the higher the contact angle, the greater the hydrophobicity of the nanofiber sheet.

Experimental Methods

Styrene-butadiene-styrene triblock copolymer, purchased from Sigma-Aldrich containing 21% styrene by weight, and styrene-isoprene-styrene triblock copolymer, purchased from Sigma-Aldrich containing 21% styrene by weight, were used throughout the course of experiments for this project. Each polymer was supplied in the form of rubbery pellets. The difference between these two copolymers is the main repeat unit in the linear polymer chain. 1,3-butadiene polymerizes into two conformations of 1,4-polybutadiene and 1,2-polybutadiene. Isoprene may also be referred to as 2-methyl-1,3-butadiene and polymerizes in much the same fashion. Tetrahydrofuran (THF) and n,n-dimethylformamide (DMF), both purchased from Fisher Scientific, were used as solvents in the preparation of the polymer solutions and were used at a ratio of 75:25 THF:DMF by weight. The polymers and solvents were used as is and were not purified further.

Polymer solutions of SBS copolymer and SIS copolymer were prepared at using THF and DMF in the above weight ratio at concentrations of 11% and 12% SBS by weight using 2g of SBS and variable weight concentrations between 10% and 15% SIS using 2g to 3g of SIS. The solutions were prepared in glass vials containing magnetic stir bars, sealed with plastic wrap, and placed on a hot plate set to 40°C and allowed to stir until clear polymer solutions were observed. The solutions were not allowed to stir overnight to avoid variability in prepared polymer concentration and electrospinning polymer concentration caused by solvent evaporation.

Once fully dissolved, the samples were electrospun using variable electric potential and flow rate of polymer solution. A schematic of a typical electrospinning setup is shown below.

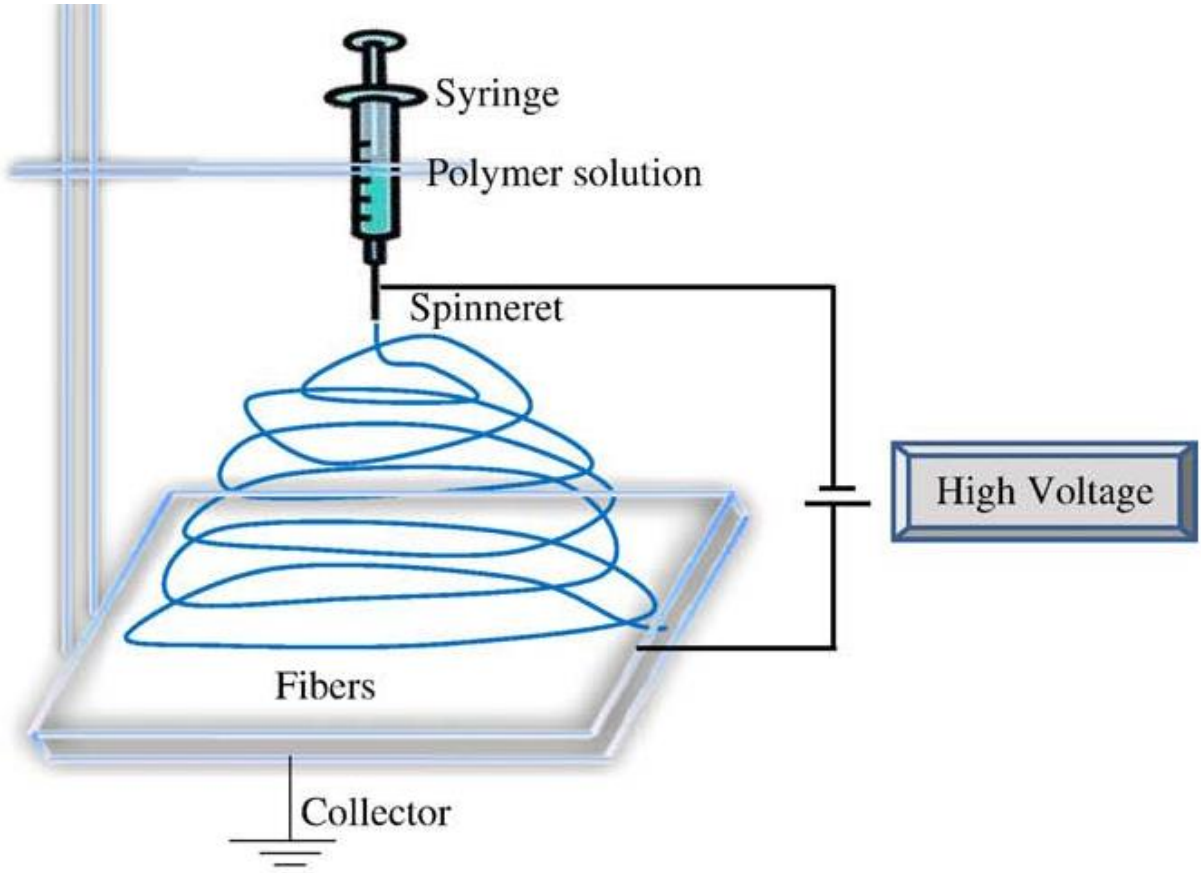

Figure 1: Typical electrospinning setup [3].

A variable high voltage power supply with a range of 0 to 30kV was used to apply the electric potential to the polymer solution. The solution is held in a 5mL luer lock syringe and extended using plastic tubing. The needle tip is attached to the high voltage power supply and placed 25cm above the grounded sheet of aluminum foil used as the metal collector. The flow rate of the polymer solution through the charged needle is controlled via a syringe pump. Flow rates were chosen at 25mL/h and 15mL/h with a voltage of 30kV and voltages were chosen at 30kV and 25kV with a flow rate of 25 mL/h for experimentation. A summary of the SBS and SIS electrospinning conditions is given below. It should be noted that the supply of SBS copolymer was limited and the product has been discontinued. Therefore was placed under less priority than the SIS copolymer.

Table 1: Operating parameters for electrospinning of SBS and SIS triblock copolymers.

Sample #	Copolymer	Concentration (wt%)	THF:DMF Ratio (wt:wt)	Voltage (kV)	Volumetric Flow Rate (mL/h)
1	SBS	12%	75:25	30	25
3		11%	75:25	30	25
5		12%	75:25	25	25
6		11%	75:25	25	25
7		12%	75:25	30	15
8		11%	75:25	30	15
9	SIS	10%	80:20	30	25
10		10%	75:25	30	25
11		12%	75:25	30	25
12		11%	75:25	30	25
13		12%	75:25	25	25
14		11%	75:25	25	25
15		12%	75:25	30	15
16		11%	75:25	30	15
17		14%	75:25	30	25
18		14%	75:25	30	15
19		15%	75:25	30	25
20		15%	75:25	30	15
21		14%	75:25	25	25
22		15%	75:25	25	25

The hydrophobicity of the nanofiber sheets were examined using the EasyDrop Contact Angle Measuring Instrument purchased from Krüss GmbH (model number FM40) and the accompanying drop shape analysis (DSA) software. During the electrospinning process, glass slides were placed on the aluminum foil collector and allowed to accumulate nanofibers until a layer of fibers was apparent on the slide. The slides were then placed on the manual sample table and then centered on the camera. 5µL water droplets were dispensed using the DSA software and a microliter syringe fixed to the instrument. Once focused, the contact angle of the water droplets were easily calculated using the DSA software and were averaged using multiple calculations and multiple sampling positions on the nanofiber sheet.

The nanofibers were analyzed using the TM3000 scanning electron microscope made by Hitachi and its accompanying software. Double sided electrical tape was placed on a metallic base and used to pick up a portion of the nanofibers from each sample. Several images were taken of each sample to obtain an average nanofiber diameter. The Fibraquant software (version 1.3) was used to analyze each SEM picture and to measure the nanofiber diameters of a selected area of each picture.

Data and Results

Table 2: Nanofiber characterizations for SBS and SIS triblock copolymers.

Sample #	Copolymer	Fiber Diameter (μm)		
		Average	Std Dev	Median
1	SBS	1.968	1.042	1.845
3		Unable to Characterize		
5		2.222	1.050	2.155
6		2.287	0.931	2.153
7		3.701	1.563	3.798
8		2.267	0.985	2.279
9	SIS	Unable to Characterize		
10				
11				
12				
13				
14				
15				
16				
17		1.199	0.518	1.159
18		0.867	0.359	0.824
19		1.027	0.411	0.998
20		1.167	0.462	1.145
21		1.038	0.456	0.990
22		2.107	0.705	2.067

Table 2 details the nanofiber dimensions achieved through each electrospinning condition in Table 1. Sample 3, the 11wt% solution of SBS, was unable to be characterized because when placed in the electrospinning setup, the solution electrowetted onto the aluminum collector. That is to say, the solution was not stretched into threads but rather flow viscously through the needle tip. Samples 9 through 16 contained 11wt% and 12wt% solutions of SIS in 75:25 wt:wt solvent mixture of THF:DMF. These solutions, once analyzed under SEM, did not form nanofibers. Instead, microscale particulates of the SIS triblock copolymer were coated onto the aluminum collector. An example SEM image of sample 9 may be seen below.

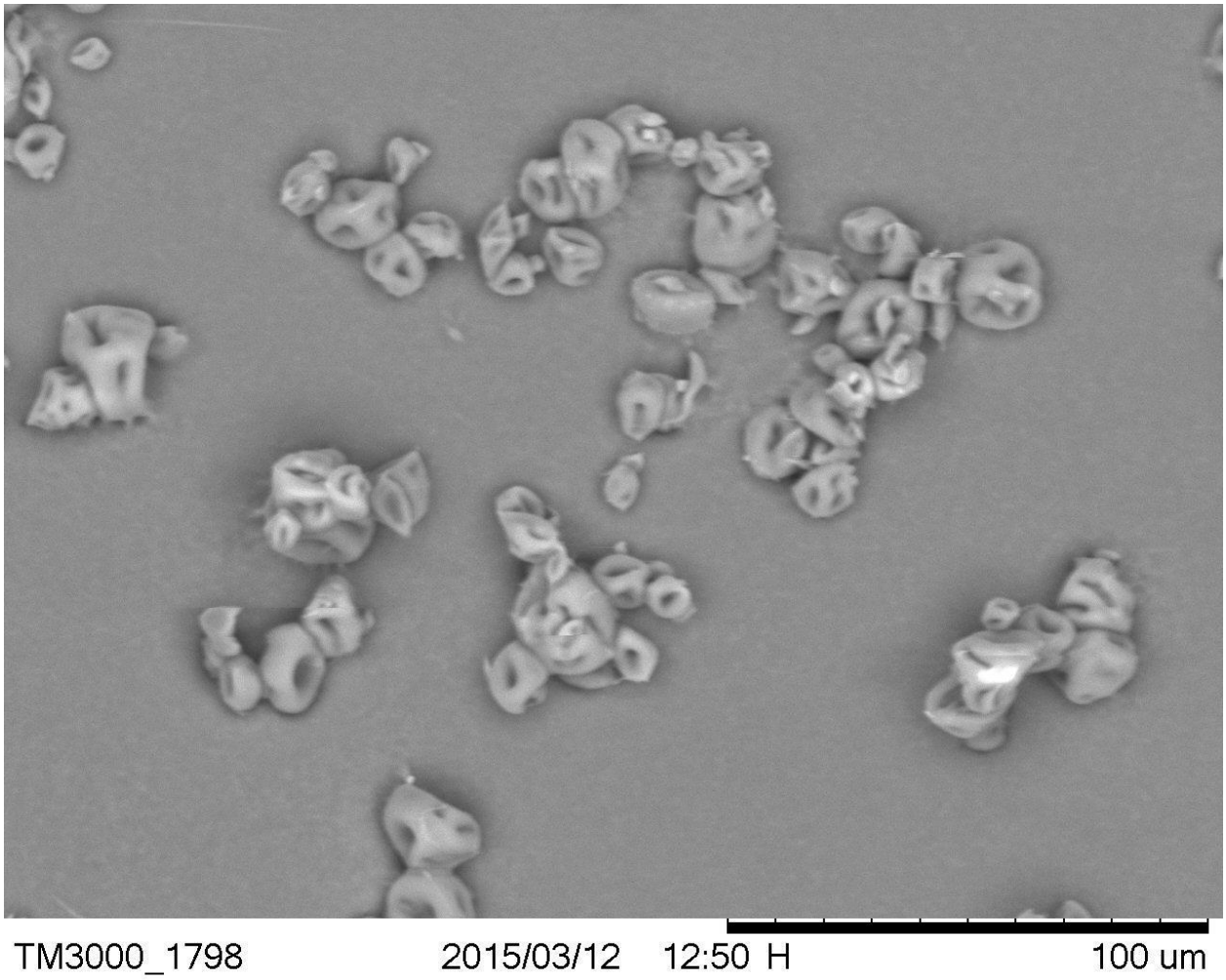

Figure 2: SEM image of SIS microscale particulates produced from 10% SIS polymer solution.

When the polymer concentration in the solution was increased to 14% and 15%, nanofibers were successfully electrospun. Examples of SIS nanofibers produced at varying conditions are shown below.

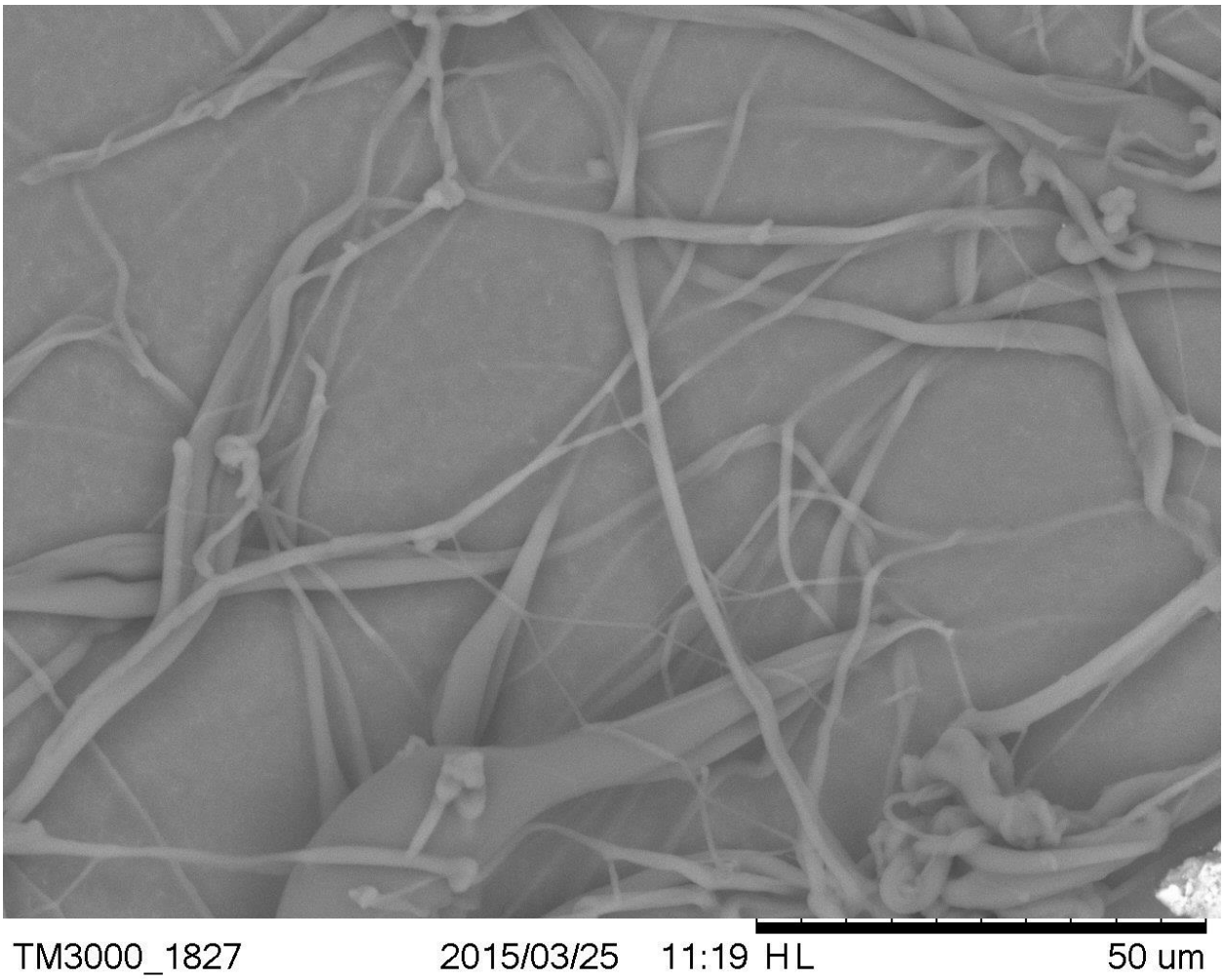

Figure 3: SIS nanofibers produced using 14wt% solution in 75:25 THF:DMF at 30kV and 25mL/h.

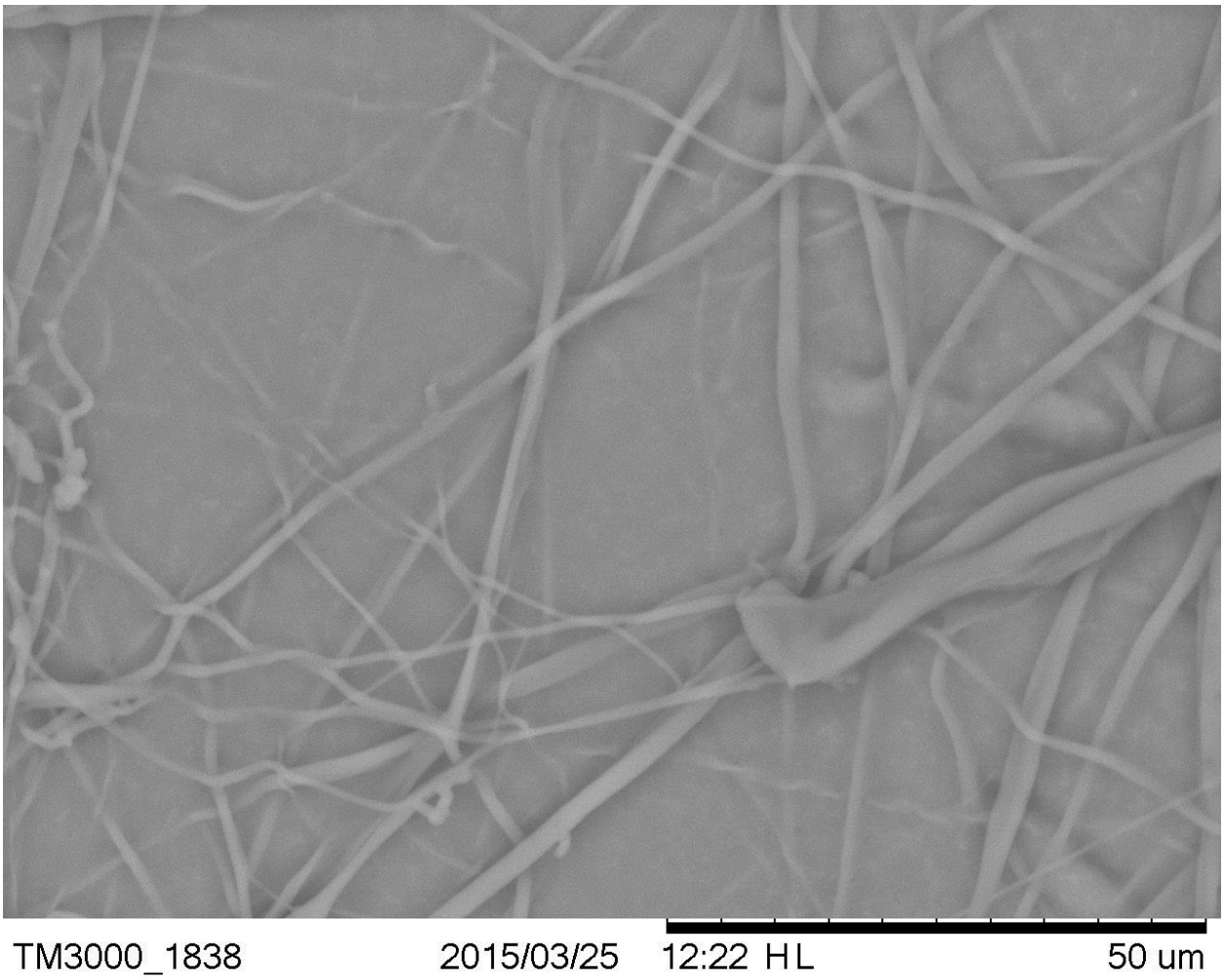

Figure 4: SIS nanofibers produced using 15wt% solution in 75:25 THF:DMF at 30kV and 25mL/h.

The contact angle of 5μL water droplets were analyzed using the Krüss EasyDrop apparatus. The data collected from the nanofiber sheets of SIS triblocks as well as the electrosprayed SIS samples is shown below along with a graphical representation of the relationship between the water droplet contact angle and the average nanofiber diameter.

Table 3: Water droplet contact angles for SIS triblock electrospun sheets.

Sample #	Average Nanofiber Diameter (μm)	Contact Angle (deg)
9	Unable to Characterize	136.2
10		136.1
11		104.7
12		122.8
13		123.6
14		121.0
15		130.7
16		126.9
17	1.199	118.6
18	0.867	118.1
19	1.027	131.3
20	1.167	122.4
21	1.038	124
22	2.107	Unable to Measure

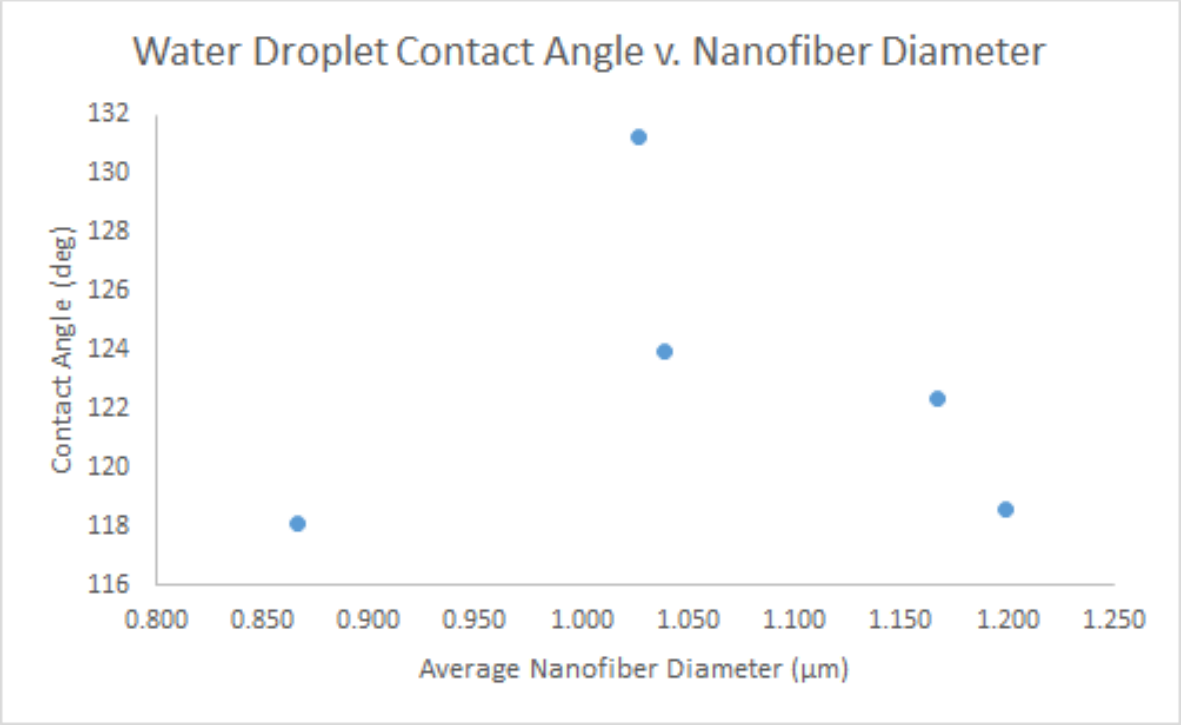

Figure 5: Scatterplot of contact angle and nanofiber diameter data for SIS triblock sheets.

Discussion/Analysis

It appears evident from Table 2 that the substitution of the isoprene repeat unit for the butadiene unit in the triblock assisted in the electrospinning of smaller nanofibers. In addition to achieving a smaller nanofiber diameter, the SIS triblock also formed a more uniform nanofiber sheet, with standard deviations in nanofiber dimensions at roughly half of those from the SBS triblock. It is difficult to determine if the decreased nanofiber dimensions are primarily influenced by the substitution of isoprene for butadiene in the polymer chain or if supplementary influences exist. Unfortunately, not much information is given for these two copolymers besides repeat unit composition and styrene content. The styrene content of each copolymer is very similar, differing by only 1%, so it may be assumed that the styrene content difference is negligible. The number average molecular weight and weight average molecular weight may be significantly different for these two polymers, which would influence the electrospinning parameters. Humidity also plays a large factor in electrospinning parameters and nanofiber characteristics. According to Cheryl L. Casper et al, electrospinning in an atmosphere of less than 25% humidity produced smooth fibers without any surface features, while increasing humidity above 30% produced pores on the surface of the fibers. Higher molecular weight solutions cause the fibers to contain large pores that are less uniform in shape and size [8]. The lab in which the polymer solutions were electrospun was not climate controlled and the humidity was not able to be measured. Additionally, the temperature was not measured during each electrospinning session. Furthermore, the distribution of the chain conformations of the butadiene and isoprene repeat units is not known. These chain conformations impact both viscosity and glass transition temperature by allowing the polymer chains to more readily pack together in lattice structures.

Figure 3 displays the water droplet contact angle data for the SIS nanofibers. There appears to be an inverse parabola trend in which the water contact angle peaks with nanofibers of average width of around 1.025 μm. However, the data in Table 3 implies the electrospun samples that produced the microscale particulates of SIS produced sheets with a greater hydrophobicity. It is unsure as to why this phenomenon occurred. Error may also be present in the water contact angle data collected. Uneven films of electrospun nanofibers on the glass slides may have skewed the data for each nanofiber sheet.

Conclusions

At this point, a conclusion as to whether or not to use the SIS triblock copolymer for use in the filtration of water out of fuels is unable to be reached. It is recommended to continue research into the electrospinning of SIS triblock copolymers at varying styrene content to determine the effect of styrene content on the electrospinning process and nanofiber properties. It is also recommended to research other elastomeric copolymers to find a balance between monomer properties that will allow for adequate filtration properties.

References

1. Dawar, S. Water Contamination in Fuel: Cause and Effect - American Filtration and Separations Society http://www.afssociety.org/automotive/93-water-contamination-in-fuel-cause-and-effect (accessed Mar 25, 2015).
2. Li, Z.; Wang, C. *One-Dimensional Nanostructures: Electrospinning Technique and Unique Nanofibers*; Springer-Verlag Berlin and Heidelberg GmbH & Co. KG: Germany, 2013.
3. Bhardwaj, N.; Kundu, S. C. *Biotechnology Advances* **2010**, *28* (3), 325–347.
4. Feng, S.; Shen, X. *Journal of Macromolecular Science, Part B* **2010**, *49*(2), 345–354.
5. Feng, S.-Q.; Shen, X.-Y.; Fu, Z.-Y.; Ji, Y.-L. *Journal of Applied Polymer Science* **2009**, *114* (3), 1580–1586.
6. Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. *ChemInform* **2003**, *34*.
7. Yuan, Y.; Lee, R. T. *Springer Series in Surface Sciences* **2013**, 3–34.
8. Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, B. D.; Rabolt, J. F.*Macromolecules* **2004**, *37* (2), 573–578.