NDnano Summer Undergraduate Research
2016 Project Summary

Student name: Manikandan Suresh
Birla Institute of Technology, Mesra
Email id: manikandan.mech2k14@gmail.com

Faculty mentor name: Prof. Tengfei Luo
Assistant Professor
Department of Aerospace and Mechanical Engineering

Fabrication of polymer nanofibers with anomalous thermal conductivity

Summer research at the university of Notre Dame gave me first hand experience of cutting edge research. During my 8 weeks of stay here, I realized that patience and perseverance are the 2 key pillars of scientific progress. I learnt to work and collaborate with other group members and another NURF student to succeed in the project goals. I acquired several skills in experimental research like setting up the apparatus required for the experiment, analyzing the failures to identify solutions and proactive study of existing literature.

Practical application/end use:

Thermal management is a major bottleneck in several industries, for example in computers and servers. Currently, metals and thermoelectric materials are primarily being used to transfer heat and manage thermal budget. My research involves fabrication of thermally conductive polymer nanofibers that hold the potential to be a low weight, chemically resistant and cost effective replacement to existing solutions. Furthermore, novel thermal devices can be envisioned if intrinsic thermal anisotropic nature of polymeric chains due to structural anisotropy is investigated and utilized.

Project summary:

Introduction

In this work, my goal was to find the optimum conditions to achieve several millimeter long fibers with sub-micron diameters. Such small diameters of fibers are essential to avoid voids in the polymer matrix and entanglement of polymer chains, which could prove detrimental for mechanical and thermal properties. Fabrication of polymer nanofibers involves 2 broad steps namely, preparation of polymer gel and drawing the fiber from the gel. Parameters that affect the gel preparation are: concentration of the Polyethylene-Decalin mixture, temperature of gel preparation, revolutions per minute of the magnetic stirrer, nitrogen supply rate, duration of quenching and heating. The draw rate and temperature during drawing affect the length and the

diameter of the fiber drawn. During the process of drawing the fiber, the diameter decreases with increasing length of the drawn fiber. This acts to our advantage by applying a uniaxial strain on the polymer chains resulting in a better alignment. Using previously published results [1,2] as a starting point, we explored a range of parameters as presented below to successfully demonstrate high aspect ratio fibers as desired.

Protocol Followed

The Polymer Gel Suspension

To fabricate a Polyethylene (PE) nanofiber, we first dissolve PE powder in the Decalin solvent at 70 °C forming a solution of 0.8 wt% concentration. Then the solution temperature is ramped to 160°C in ~5 mins and then lowered to 140°C, where its held stable. During this process PE dissolves completely in Decalin. This process of dissolution takes 11 minutes and is conducted in a three way round bottom flask with nitrogen gas to avoid molecular degradation. After the white PE powder is completely dissolved, the mixture becomes a transparent viscous fluid and the round bottom flask containing the liquid is immediately quenched in a cold water bath. When the liquid is cooled down to room temperature, the translucent PE gel is made.

Polymer fiber drawing

Following the PE gel preparation, a two-stage heating process is implemented to produce highly-crystalline PE nanofibers. A hot plate is used to uniformly heat the air above at 70-80 °C. A silicon chip is suspended about 1 cm over the hot plate. A small heater is attached to the back of the chip. The heater and the chip together form a PE gel holder whose temperature can be adjusted to melt the gel in a controllable period of time. Gel droplet whose diameter approximately measuring $1/8^{th}$ of an inch is placed upon the holder and is heated up to 120 °C on the silicon chip for a few seconds until the translucent gel turns into a clear liquid. A micrometer-diameter tungsten tip fixed to a micromanipulator is then used to horizontally pull a microfiber with a length of few millimeters. The microfiber suspended over the hot plate is heated by the hot air. The microfiber is then slowly drawn so that its size is scaled down to nanometer level, and during this drawing process, the fiber is subjected to the second stage heating which reaches to a maximum temperature of 130°C. A mixed elongational and shear flow is observed during the drawing process. The pulling velocity is on the order of 10-50 $\mu m \cdot s^{-1}$. After the fiber has been elongated to the desired length, the tungsten drawing needle is moved in the forward direction in order to release some tension in the fiber. The entire fabrication process is conducted under a dark-field stereo microscope having a magnification of 25X and takes 1 ~2 minutes. The uniformity of nanofibers can be improved by using a lower pulling velocity. However, with the same shear duration, a higher pulling velocity generally results in a larger shear rate and a smaller diameter of a nanofiber. Once the nanofiber is drawn, all the heating elements are turned off and the fiber is allowed to cool down to room temperature (approximately 2 mins). Then the diameter of the specimen is measured by shifting the specimen to another microscope having greater magnification (40X and 100X) to improve the accuracy of the measurement. The fiber attached to the tungsten tip is cut down before we shift the specimen. In order to get the fiber cut without affecting it, a tiny gel droplet is dropped gently at the tungsten tip which on cooling solidifies and holds the fiber firmly which later can be cut down and placed under objectives having higher magnification.

TEST NO.	CONC	GEL PREP	FIBER DRAWING	RESULT	REMARKS
1	1) PE: 0.023g	1) RPM of stirrer:350 rpm	1) temp: initially started drawing at 120°c and finished drawing when temperature was close to 130°c	1) length of fiber measured: 10 mm	
	2) Dec: 3ml	2) Temp: added the solution at 70°c and allowed it to spike up to 160'c, later maintained at 140°c	2) surrounding temperature: 70°c	2) minimum diameter: 3.4 µm	
	i.e. wt % = 0.8%	3) Time: 11 mins	3) draw rate: maximum velocity: 0.03mm/sec	3)maximum diameter: 16.2 µm	
		4) nitrogen supply: kept as low as possible	4) maximum acceleration: 0.01 mm/sec		
		5) quenching: ice quenched, 3 mins			

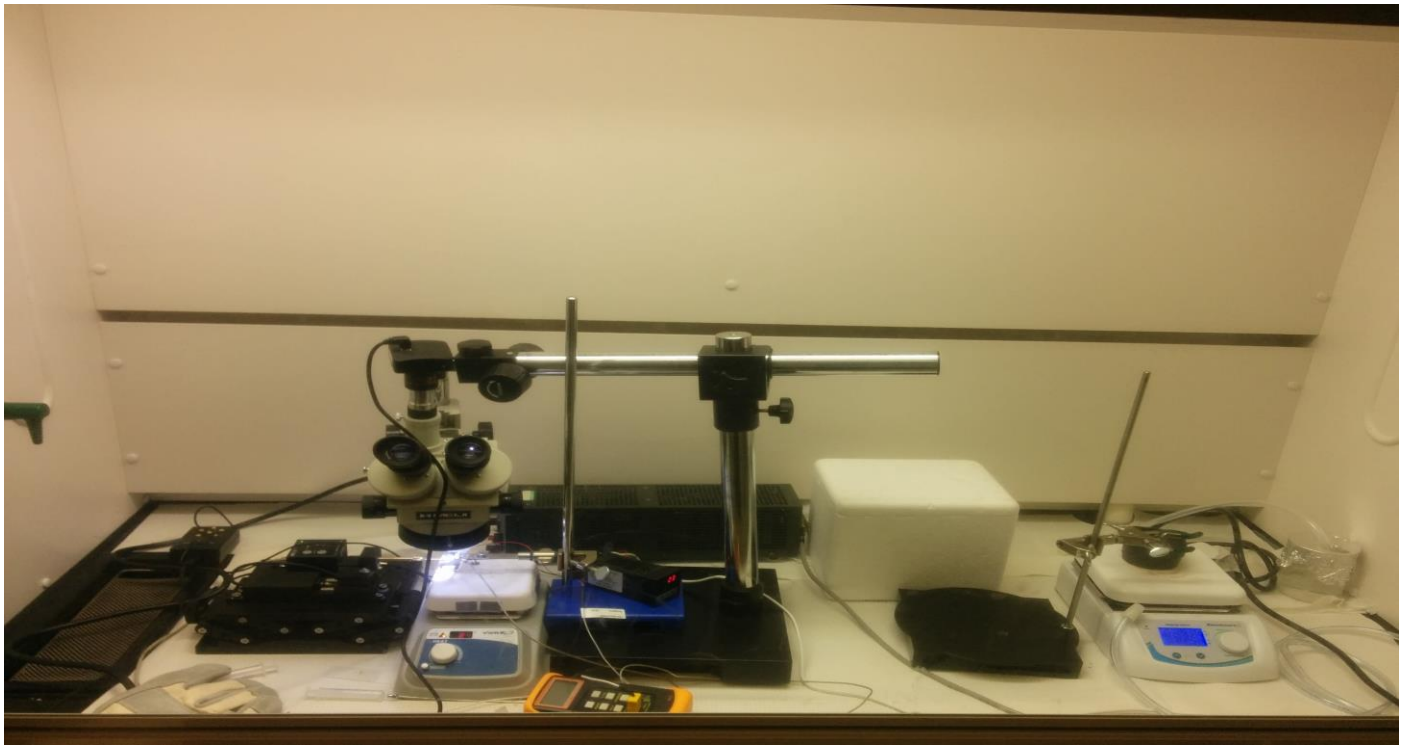


Figure 1*. (a) Complete Fiber drawing and gel preparation set up within the fume hood.*

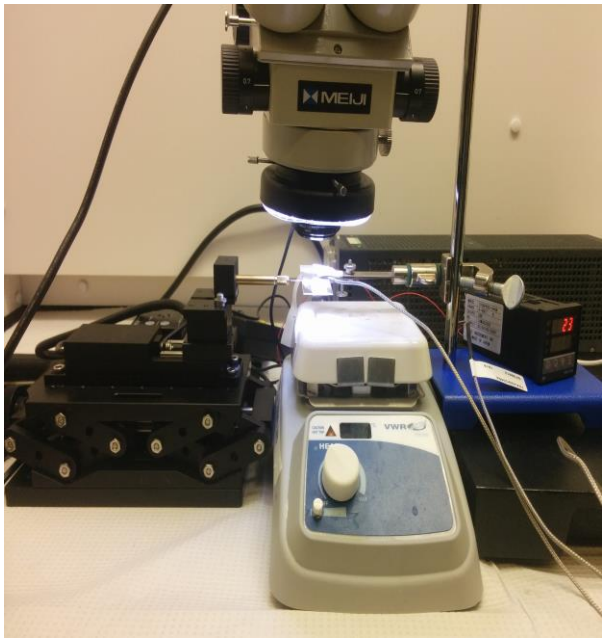


Figure 2*. (a) Microscope used to measure fiber diameters using objectives of higher magnification. (b) Drawing apparatus comprising the tungsten tip fixed to a micromanipulator, thermocouple, microscope and the heater.*

Results and Observations

TABLES

PE/Decalin mixing ratio

mL of Decalin	Mass of Decalin (g)	Mass of PE (g)
0	0	0
1	0.896	0.007225806
2	1.792	0.014451613
3	2.688	0.021677419
4	3.584	0.028903226
5	4.48	0.036129032
6	5.376	0.043354839
7	6.272	0.050580645
8	7.168	0.057806452
9	8.064	0.065032258
10	8.96	0.072258065

Table 1 *– shows the mass of PE needed to be mixed in with Decalin to form the gel. To calculate take a volume of Decalin and convert it to mass using the density of Decalin, 0.896 g/mL. Next, take the mass of Decalin and multiply it percentage weight of PE (0.8) and divided by (100 - (percentage weight of PE)).*

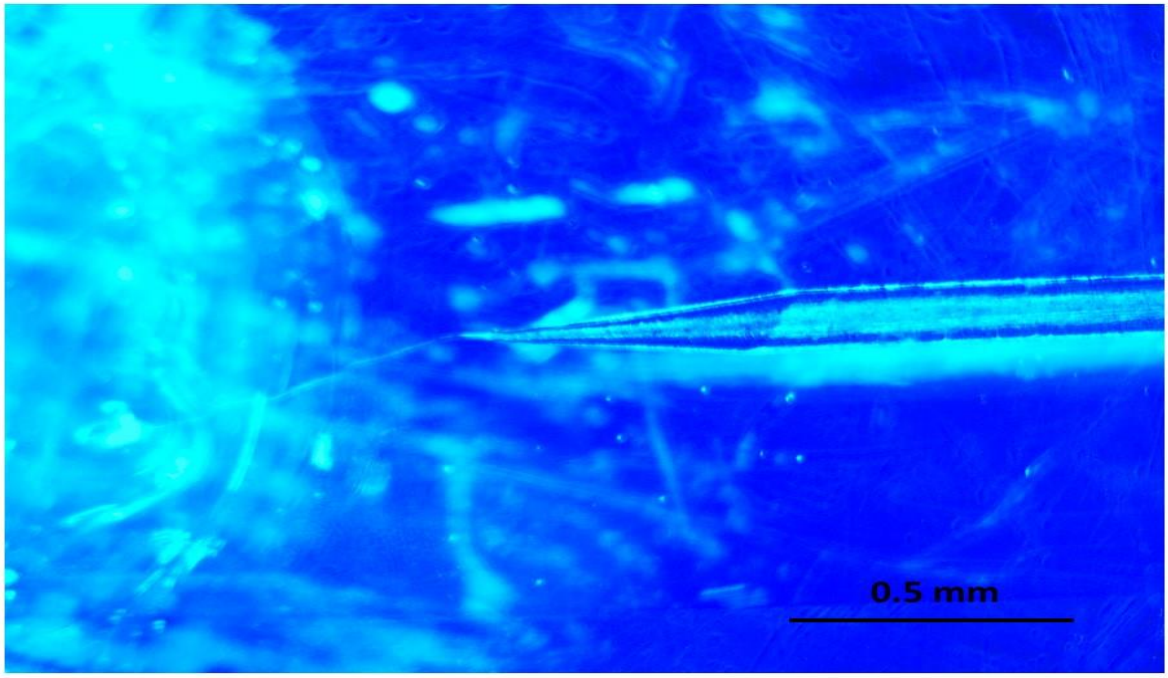
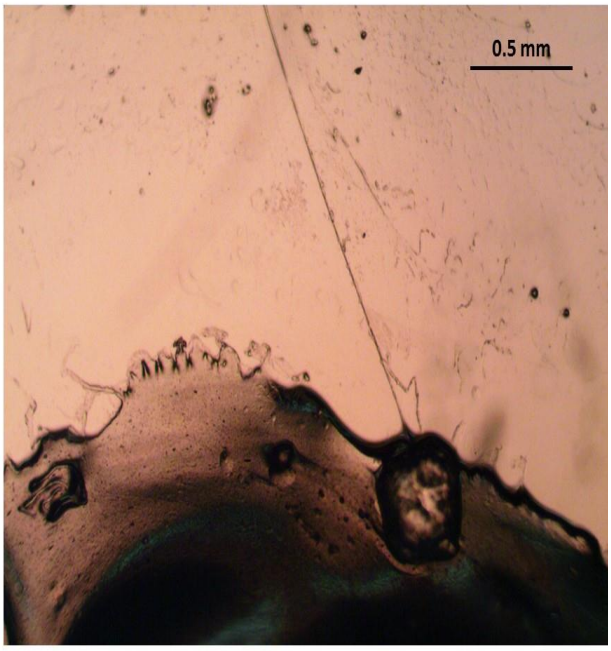


***Figure 3**. A fiber being drawn from a Polyethylene-Decalin gel.*



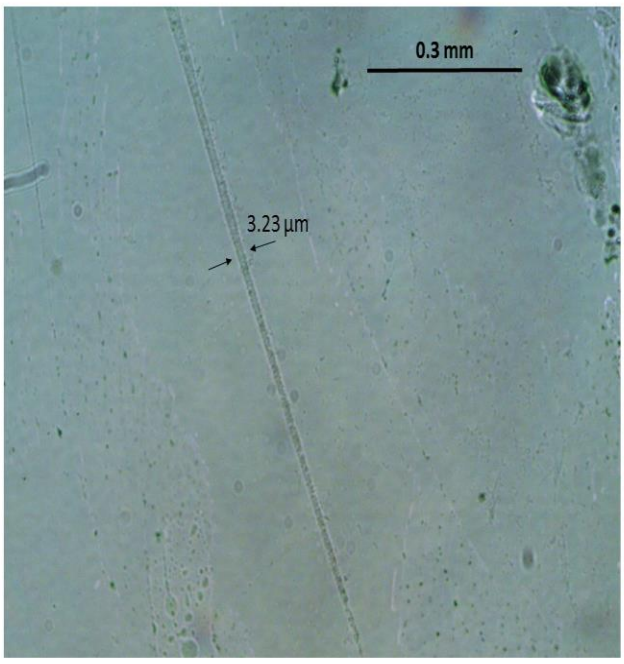


***Figure 4**. (a) A polyethylene fiber under 10X magnification. (b) A polyethylene fiber under 40X magnification.*

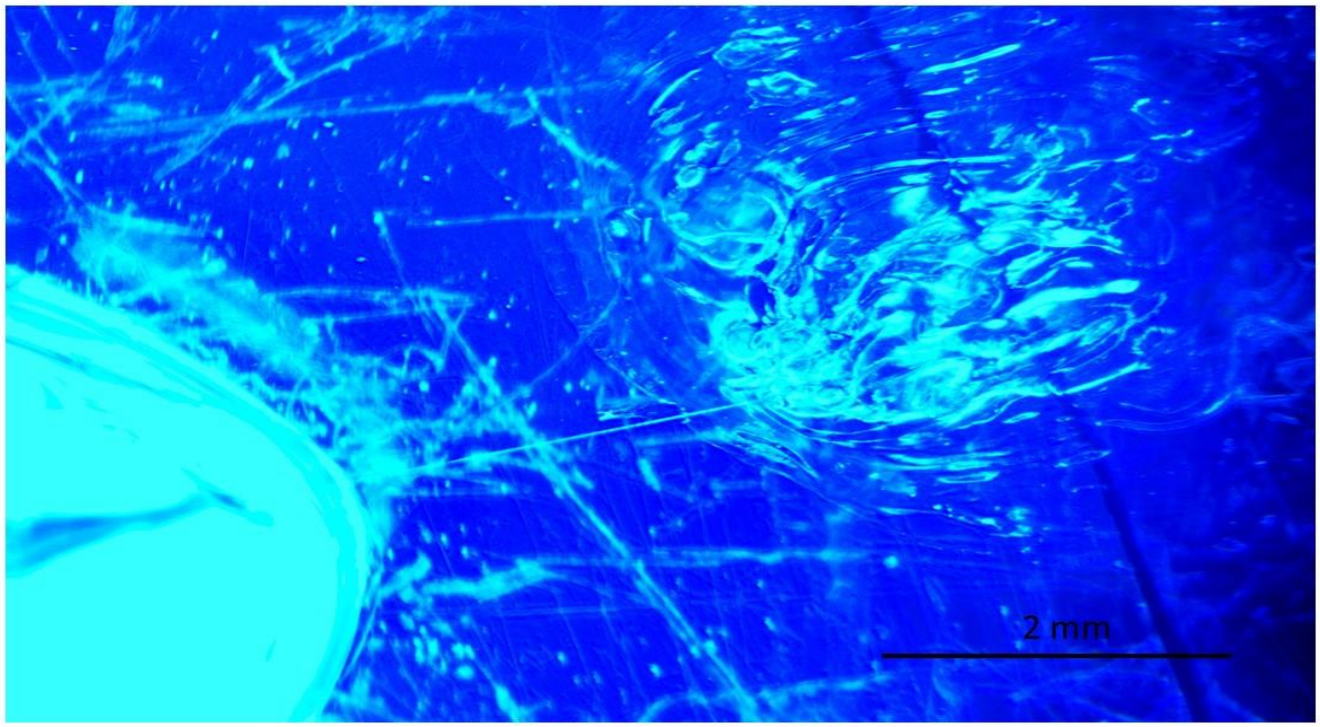


Figure 5. *A second gel droplet is gently dropped at the tungsten tip such that the fiber drawn merges with the gel which when cooled down eases the process of cutting down the fiber.*

References

1) Crystalline Polyethylene Nanofibers with the Theoretical Limit of Young's Modulus
Pengfei Li, Lin Hu, Alan J. H. McGaughey, and Sheng Shen

2) Polyethylene nanofibres with very high thermal conductivities
Sheng Shen, Asegun Henry, Jonathan Tong, Ruiting Zheng, and Gang Chen