Training Undergraduate Engineering Students on Biodegradable PCL Nanofibers through Electrospinning Process

Shawn M. Hughes, Anh Pham, Kathy Huong Nguyen and Ramazan Asmatulu*

Department of Mechanical Engineering, Wichita State University
1845 Fairmount, Wichita, KS 67260-0133, USA
**Email: ramazan.asmatulu@wichita.edu*

Abstract

Nanotechnology has a great potential to revolutionize the industrial and scientific realm of knowledge. Electrospinning is one of the most effective techniques to fabricate nanotechnology products, such as nanofibers, nanomembranes, nanofilms and nanocomposites for different industrial applications. In the present study, an electrospinning technique was used to fabricate nanofibers using polycaprolactone (PCL) after dissolving in acetic acid ($HC_2H_3O_2$) and acetonitrile (C_2H_3N) at a 50:50 wt% ratio. The produced PLC nanofibers can be used in different industrial and research applications, including scaffolding, energy storage and conversion, drug delivery, bio and nanosensors, filtration, and so on. During the experiments, two female undergraduate students in the Department of Mechanical Engineering were trained to produce these PCL nanofibers. It is believed that these hands-on experiences will motivate students to do more advanced studies in the engineering fields.

Keywords: Electrospinning, Polycaprolactone (PCL), Nanofibers, Undergraduate Students, Hands-on Training.

1. Introduction

Nanotechnology has a great potential to revolutionize the scientific and industrial developments worldwide [1]. A number of different nanoscale materials in the forms of metals and alloys, polymers, ceramics and composites can be produced using nanotechnology processes (e.g., top down and bottom up approaches). These nanomaterials have various application capabilities that could greatly affect physical and chemical properties of the new materials, structural integrity, and tissue engineering, as well as research and development in engineering [2].

Electrospinning is one pf the nanotechnology processes to produce nanosize fibers. The high-electric field is used to overcome the surface tension of the polymeric solutions to produce various size and shape of nanofibers [3-7]. When the intensity of the electric field increases beyond a certain limit (also called threshold intensity), the semicircular surface of the polymer solution begins to elongate in a configuration known as a Taylor cone [8]. In the electrospinning process, the properties of a material can be vastly changed by adjusting system and process parameters, such as DC voltage, pump speed, distance, polymer and solvent types, protonation of the polymers, temperature, humidity, viscosity, surface tension, air velocity, capillary tube diameters, and so on [9-11].

For example, changing the diameters of polymer fibers can change many physical properties of the nanofibers, which can determine their final uses in different industries. The goal of the electrospinning process is to achieve a very large surface area to volume ration, which usually provides several mechanical and other physical property advantages, such as strength, stiffness and elastic modulus [1]. The outstanding properties of polycaprolactone (PCL) nanofibers can make the fibers a perfect candidate for many industrial applications.

Although the term electrospinning was used relatively recent because of the new developments in nanotechnology processes, its fundamental idea dates back to 1934 to 1944 where the company Formhals published a series of patents [12-15], describing an experimental setup for the production of polymer filaments using an electrostatic force [4]. However, it was not until 1969 when Tyler studied the polymeric droplet demonstrating that at the tip of the capillary a stream was ejected from the vertex of the cone [8]. Based on Tyler's observations, the researchers around the world focused on electrospun fiber fabrication and characterization processes in detail [3-7].

The electrospinning is relatively easy process compared than other nanotechnology processes currently being used in the industry, such as wet spinning, extrusion molding, and melt spinning. The solution developing from the capillary, called capillary stress, has a stress ratio well-defined as γ/r, a ratio where γ would be the surface tensions and r the radius of the meniscus that developed at the end of the capillary tube. This stress defined by Maxwell stress tensor can be defined as [3-5];

$$\sigma_{ij} = \varepsilon V_i V_j \frac{1}{\mu} B_i B_j - \frac{1}{2}(\varepsilon V^2 + \frac{1}{\mu_0} B^2)\delta_{ij} \tag{1}$$

where ε is the permittivity, V is the applied voltage (spinning voltage), B is the magnetic part and dividing by H^2, where H is the distance between the collector screen and capillary tube. The equation (1) can be reduced to the following form [5]:

$$\sigma = (\varepsilon V^2)/H^2 \tag{2}$$

Other forces acting on the polymeric solution include inertia, hydrostatic pressure, and viscoelastic forces, which have little effect compared to the high-electrostatic force. Thus, these forces can be mostly ignored. Balancing the Maxwell stress and capillary stress would yield the critical spinning voltage V_c that must be overcome to initiate electrospinning process [3]:

$$V_c = \sqrt{\frac{\gamma H^2}{r\varepsilon}} \tag{3}$$

Earnshaw's theorem applies to the primary principles of the voltage needed to be applied on a polymeric solution that will cause a mutual charge repulsion across a longitudinal stress. This would be due to the point charge not being maintained in the equilibrium. The solutions in this study were run at 15 kV DC to achieve a nanofiber. The major purpose of this experiment was to increase knowledge of the undergraduate engineering students on electrospinning process and ideology.

2. Experimental
2.1 Materials

Biodegradable PCL powder was purchased from Scientific Polymer Products Inc., while acetic acid and acetonitrile were purchased from the Fisher Scientific, and Acros, respectively. The polymer and solvents were used during the student experiments without any modifications or purifications.

2.2 Methods

2.2.1 Fabrication of PAN Nanofibers

Figure 1 shows the undergraduate students preparing the PCL solution using acetic acid and acetonitrile prior to the electrospinning process. A mixture of acetic acid ($HC_2H_3O_2$) and acetonitrile (C_2H_3N) solution was prepared with a 50:50% wt. ratios (4.5g acetic acid and 4.5g of acetonitrile). Then, 15% wt. of PCL was dissolved in the solution using 10 minutes of sonication followed by 24 hours of mixing at 70° C and 500 rpm. After 24 hours of mixing, the solution was put into a 10 ml syringe with a metal needle diameter of 0.5 mm. A copper electrode wire, having a diameter of 0.25mm, was attached to the needle end, while the other end of the electrode was connected to the DC power supply unit. Figure 2 shows the schematic view of the electrospinning process. The nanofibers were produced at 15 kV DC on syringe and -15 kV on the collector screen at a rate of 1 ml/hr pump feed rate of the PCL solution. A separation distance of 17 cm was set from the spinneret to the collector screen.

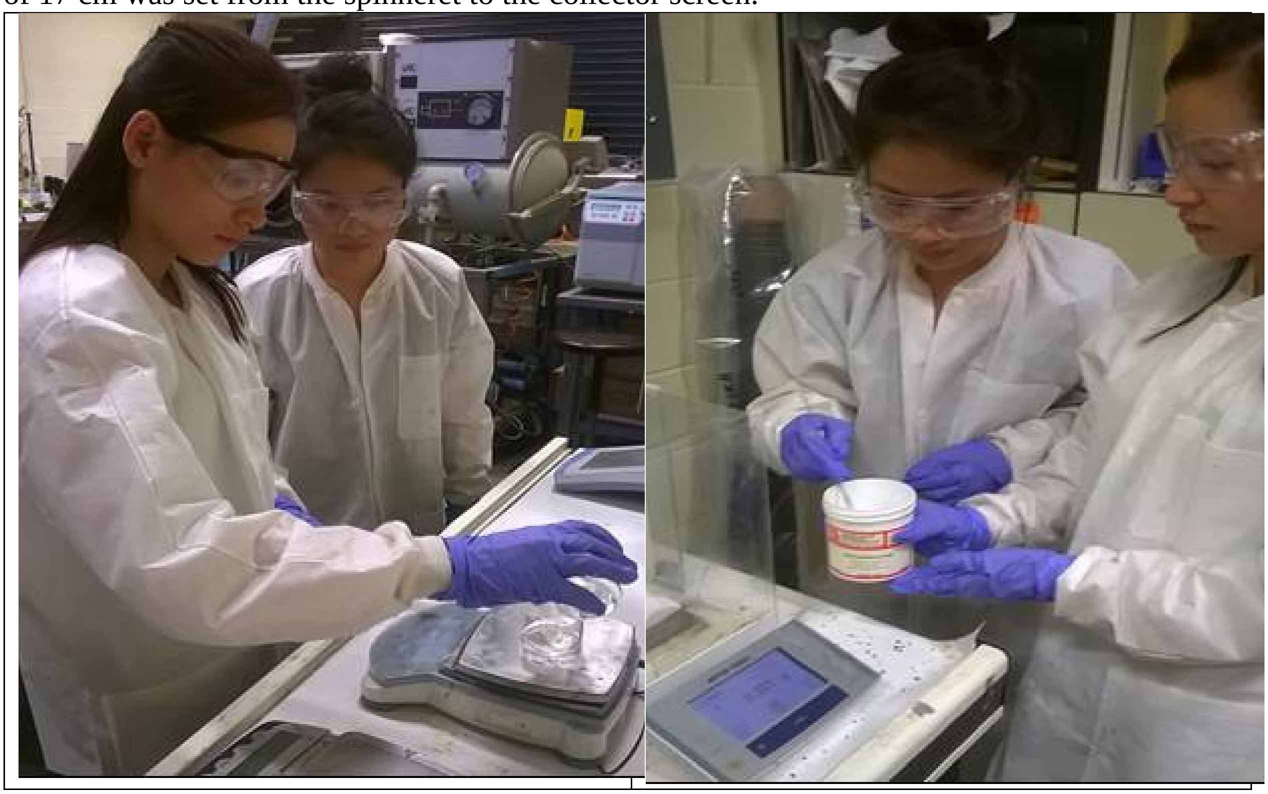

Figure 1: The undergraduate students preparing the PCL solution using acetic acid and acetonitrile prior to the electrospinning process.

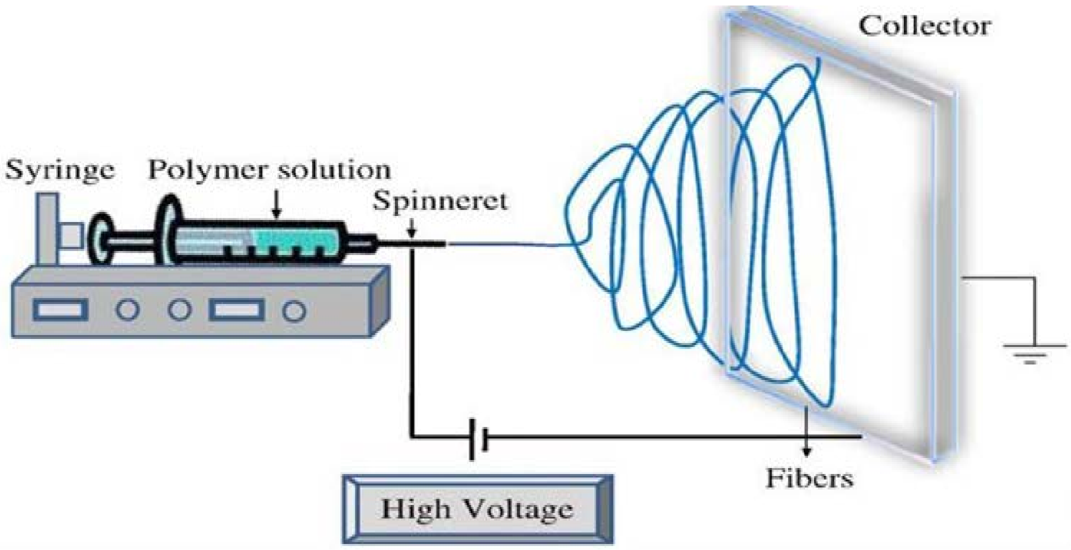

Figure 2: The schematic view of the electrospinning process used to produce the PCL nanofibers.

Figure 3 show the experimental setup of the electrospinning process in the laboratory used for the production of the PCL nanofibers. After the allotted time, the spinning process was done and the collector was removed from the chamber in order for the fiber mesh to be removed. Then, the property of the PCL nanomaterials were examined. The characteristic analysis will provide the properties, such as fiber diameter and shape, pore size, bead formations, and other properties of the produced nanofibers.

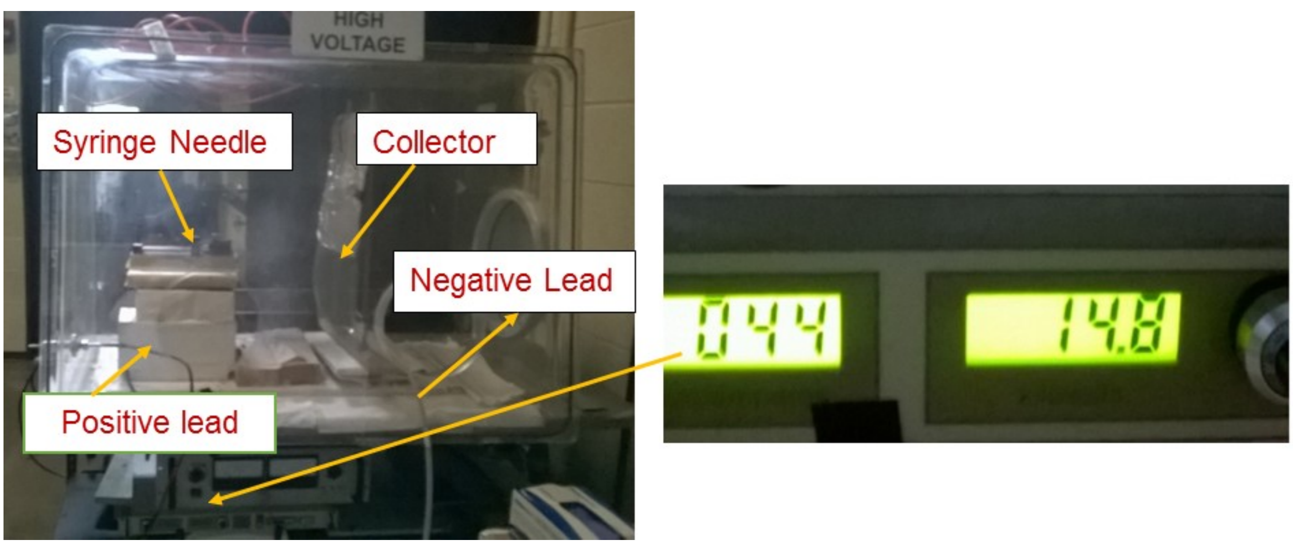

Figure 3: Experimental setup of electrospinning process for the production of the PCL nanofibers.

3. Results and Discussion

The primary aims of this study was to produce the PCL nanofibers and train the undergraduate engineering students on the electrospinning process. During the electrospinning process, the undergraduate students learned about how to create nanofibers using polymers, solvents and protonation process. Figure 4 shows the photographs of the PCL nanofibers before protonation, and after protonation processes. As can be seen, without the acetic acid protonation process, the PCL fibers were collapsed, and became a bulky PCL materials. However, in the presence of protonation process with the acetic acid, the PCL nanofibers were successfully produced by the undergraduate engineering students.

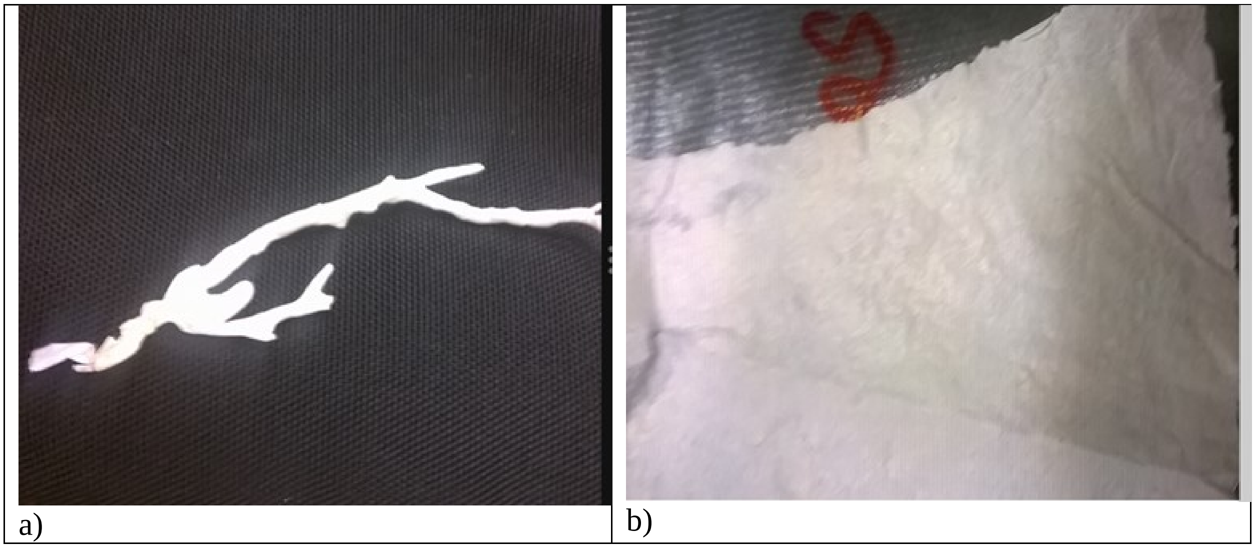

Figure 4: The photographs showing the PCL nanofibers a) before protonation, and b) after protonation processes.

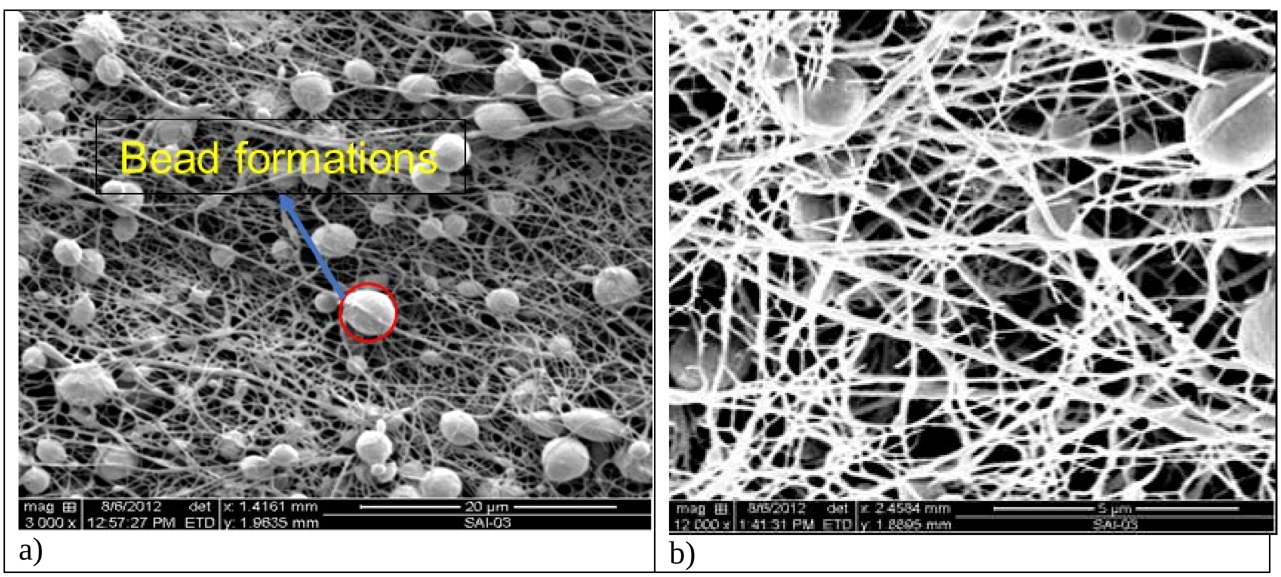

Figure 5: SEM Images of the electrospun PCL nanofibers at a) low and b) high magnifications. The bead formations (spherical particles) were clearly seen in the SEM images.

Figure 5 shows the SEM images of the electrospun PCL nanofibers at low and high magnifications. The SEM images clearly indicated that the PCL nanofibers were successfully produced after the protonation process with the acetic acid solutions. The images also indicated that different size and shape of the beads were formed during the electrospinning process. Even with the bead formations on the fibers, most of the fibers are still below 400 nm in diameter. The fibers are ununiformed and randomly dispersed. However, by controlling the process and system parameters, the PCL nanofibers can be produced without beads with a systematic uniformity and pore sizes.

There has been huge advancements in nanofiber productions in the last few years. Some of these advancements come in new processes, such as the rotating drum and translating spinnerets, electrospinning with a rotating string of electrodes, and forcespinning. Rotating drum and translating spinneret process provide an enhanced alignment, uniformity of nanofibers, and faster production rates. Also, the technique of a rotating strings of electrodes could enhance the rate of production and better alignment of the nanofibers [3-7]. These new ultrafine fibers and meshes have multiple applications in areas, including biomedical, textile, filtration, self-cleaning, energy, and many other industries. These applications will grow radically with new technological discoveries in the future.

4. Benefits of Studies for Undergraduate Students

Electrospinning has a straightforward process that allows for the production of ultrafine polymeric nanofibers in a relatively short period of time. Two female undergraduate students in the Department of Mechanical Engineering at Wichita State University (WSU) were involved in the present electrospinning study. Involving undergraduates with current university research allows them to learn new technologies, techniques, procedures, and gain crucial skills and new knowledge about the novel research processes. In this research, students learned productions, characterization and applications of electrospun nanomaterials. The students realized that the electrospinning process could be used in various industries, which motivated them towards learning more advanced technology and gaining more hands-on experiences in the field. The students in the research group used this research activity as their Engineer 2020 requirements for their degree completion. Both students are also co-authors of the present study to satisfy their interest. We have confidence that this research will motivate these students to do further studies in the engineering fields.

5. Conclusions

This hands-on nanotechnology experience introduced the basic nanotechnology and associate technologies to the undergraduate engineering students. The nanotechnology training mainly focused on processing techniques of nanofibers and wires using various process and system parameters, as well as the characterizations and potential commercial applications. Throughout the experiments, the students gained an understanding of these nanomaterials and fabrication techniques, and how they were applied in nanomaterials and nanodevice fabrication. We believe that these activities will motivate the undergraduate engineering students to do further studies in these fields for their MS and PhD degrees in the future.

Acknowledgement

The authors greatly acknowledge the Wichita State University for the financial and technical supports of the present study.

References

1. Cao, G. and Wang, Y., *Nanostructures and Nanomaterials: Synthesis, Properties, and Applications*, *2nd Edition*, World Scientific, 2011.
2. Asmatulu, R., *Nanotechnology Safety*, Elsevier, Amsterdam, The Nederland, August, 2013.
3. Doshi, J., and Reneker, D.H. "Electrospinning Process and Applications of Electrospun Fibers," *Journal of Electrostatics*, 1995, Vol. 35, pp. 151–160.
4. Nuraje, N., Khan, W.S., Ceylan, M., Lie, Y., and Asmatulu, R. "Superhydrophobic Electrospun Nanofibers," *Journal of Materials Chemistry A*, 2013, Vol. 1, pp. 1929-1946.
5. Khan, W.S., Asmatulu, R., Ceylan, M. and Jabbarnia, A. "Recent Progress on Conventional and Non-Conventional Electrospinning Processes," *Fibers and Polymers*, 2013, Vol. 14, pp. 1235-1247.
6. Asmatulu, R., Patrick, S., Ceylan, M., Ahmed, I., Yang, S.Y., and Nuraje, N. "Antibacterial Polycaprolactone/Natural Hydroxyapatite Nanocomposite Fibers for Bone Scaffoldings," *Journal of Bionanoscience*, 2015, Vol. 9, pp. 1-7.
7. Li, Y., Ceylan, M., Sherstha, B., Wang, H., Lu, Q.R., Asmatulu, R., and Li, Y. "Nanofibers Support Oligodendrocyte Precursor Cell Growth and Function as a Neuron-Free Model for Myelination Study," *Biomacromolecules*, 2014, Vol. 15, pp. 319–326.
8. Taylor, G. "Electrically Driven Jets," *Proceedings of Royal Society of London*, 1969, Vol. 1515, pp. 453–475.
9. Khan, W.S., Asmatulu, R., Rodriguez, V., and Ceylan, M. "Enhancing Thermal and Ionic Conductivities of Electrospun PAN and PMMA Nanofibers by Graphene Nanoflake Additions for Battery-separator Applications," *International Journal of Energy Research*, 2014, Vol. 38, pp. 2044-2051.
10. Khan, W.S., Asmatulu, R., Davuluri, S., and Dandin, V.K. "Enhancing the Physical Properties of Recycled Polystyrenes Incorporated with Nanoscale Inclusions via Electrospinning Process," *Journal of Materials Science & Technology*, 2014, Vol. 30, pp. 854-859.
11. Anwar, R., Vattipalli, K., Mayrah, E., Asmatulu, R., and Prasad, S. "Highly Sensitive Conductive Polymer Nanofibers for Application in Cardiac Biomarker Detection," *Advanced Science, Engineering and Medicine*, 2013, Vol. 5, pp. 633-640.
12. Formhals A., US patent No: 1,975,504, 1934.
13. Formhals A., US patent No: 2,160,962, 1939.
14. Formhals A., US patent No: 2,187,306, 1940.
15. Formhals A., US patent No: 2,349,950, 1944.

Biographical Information

Shawn M. Hughes

Mr. Hughes received his BS degree in the Department of Biomedical Engineering at Wichita State University (WSU) in 2015. He is currently MS student in the Department of Mechanical Engineering at WSU), and working on biodegradable nanomaterials for tissue scaffolding.

Kathy Huong Nguyen

Mrs. Kathy Nguyen is a BS student in the Department of Mechanical Engineering at WSU, and will graduate in May 2016. She has an interest in learning nanotechnology, biotechnology, and fabrication and characterization of biomaterials and nanomaterials for her future studies.

Anh Pham

Mrs. Anh Pham is a BS student in the Department of Mechanical Engineering at WSU, and will graduate in May 2016. She has an interest in learning nanotechnology, and biotechnology, related materials for her future studies.

Ramazan Asmatulu

Dr. Ramazan Asmatulu received his Ph.D. degree in 2001 from the Department of Materials Science and Engineering at Virginia Tech. After having the postdoc experiences, he joined the Department of Mechanical Engineering at WSU in 2006 as an assistant professor, and received his tenure and promotion to be associate processor in 2012. He is currently working with 13 M.S. and 8 Ph.D. students in the same department. Throughout his studies, he has published 76 journal papers and 166 conference proceedings, edited two books, authored 33 book chapters and 4 laboratory manuals, received 35 funded proposals, 15 patents and 34 honors/awards, presented 91 presentations, chaired many international conferences and reviewed several manuscripts in international journals and conference proceedings. To date, his scholarly activities have been cited more than 1050 times, according to the web of science.