

Optimizing the Stabilization Temperature of Electrospun PAN Fibers Used for Synthesis of Carbon Nanofibers

Zahra Yousefi, Nafiseh Koohestani, Danesh Amiri, Robabeh Abdinia, Ata Kamyabi-Gol, Elham Kamali-Heidari*

Department of Metallurgy and Materials Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.

Received: 27 October 2020; Accepted: 2 February 2021

* Corresponding author email: ekh@connect.ust.hk

ABSTRACT

Electrospinning, stabilization and carbonization are three steps of synthesizing electrospun carbon nanofibers (CNF), using polyacrylonitrile (PAN) precursor. In this study, the effect of the stabilization temperature was studied on the morphology and chemical state of the electrospun PAN fibers, which were later carbonized to produce carbon nanofibers. The stabilization was carried out on electrospun PAN fibers, at different temperatures of 230 °C, 240 °C, 250 °C and 280 °C for 2h with a heating rate of 2 °C/min. Fourier transform infrared spectroscopy was used to inspect the progress of stabilization reactions. The crystallinity and composition was studied by X ray diffraction and scanning electron microscopy was used to observe the morphology of the fibers. The results showed that 230 °C is the best stabilization temperature in which not only all expected reactions take place but also the fibrous morphology is preserved. Higher temperatures led to destruction of the fibrous morphology.

Key words: Electrospinning, PAN, Stabilization, CNF.

1. Introduction

Electrospinning is one of the many methods of synthesizing polymer and composite fibers. In this method, an electrostatic field is used to produce fine fibers. During electrospinning, a high voltage applied between the nozzle and the collector forces the injected polymer solution or melt to form a liquid jet and deposit on the collector surface with a high speed. Fibers are produced when the solvent is removed or melt is solidified. The solution conductivity and concentration, as well as the solvent polarity, and molecular weight significantly affect the morphology of the electrospun fibers[1]. Electrospinning provides fibers with diameters ranging from micro to nanometers[2]. Various parameters including the solution concentration

and flow rate, working voltage, distance between the nozzle and collector *etc.* have significant influence on the diameter of the fibers in the electrospinning process[3] Decreasing the diameter of electrospun fibers will reduce the porosity fraction, while improving the fibers density and mechanical properties[1,2]. The electrospun fibers have promising properties such as high aspect ratio, high surface area, excellent electrical properties as well as high flexibility and strength[4]. Owing to these exceptional properties electrospun nanofibers have a wide range of applications in various areas ranging from biomedical applications such as drug delivery systems, antibacterial agents and wound dressing synthetic materials[2], to energy storage and conversion applications in

supercapacitors and batteries as well as catalysis[5], filtration, adsorbents[2,6], super paramagnetic field responsive materials, and mechanical reinforcement[2]. Carbon nanofibers (CNF) are among materials that are of interest to researchers and could be produced at a relatively low cost using electrospinning method. CNF can be synthesized using different precursors such as Polyacrylonitrile (PAN), Polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and pitch[7-9]. PAN is a polymer with relatively good solubility, high density, high melting point due to the presence of nitrile groups and semi-crystalline structure[10,11]. The Ultimate tensile strength, Young's modulus and density of electrospun CNFs based on PAN are between 3-7 GPa, and 1.75-2 g/cm³, respectively[12]. Electrospun CNFs have high specific surface area, high aspect ratio, excellent conductivity as well as promising mechanical properties[13]. Electrospun CNFs are used in energy storage devices such as batteries and supercapacitors because of their exceptional electrochemical performance [8,14]. CNFs are also used in solar cells because of their electrocatalytic activity[15]. CNFs are excellent catalysts due to their mechanical and chemical stability and they are also suitable for filtration, fuel cells and sensor applications[14,16,17]. In addition, CNF matrix composites are suitable materials for EMI-shielding applications because of their high electrical conductivity and small diameter[18]. Electrospun Carbon nanofibers are produced in three steps: (1) Electrospinning of the PAN containing solution (2) stabilization of the electrospun PAN fibers and (3) carbonization to achieve CNFs. Different parameters in each of the aforementioned steps affect the properties of the final product. Temperature, duration and heating rate are the most important parameters in the stabilization and carbonization steps[16,18,19]. Stabilization of PAN is typically carried out between 180-300 °C[10] while carbonization is carried out between 500-3000 °C[8,10]. During the stabilization of the PAN cyclization, dehydrogenation, oxidation and cross-linking reactions happen. The stabilization conditions should be well controlled in order to have all the reactions taken place. If the temperature or time is, too low stabilization will not be complete, while high temperatures might lead to fibers melting. Carbonization should be carried out under oxygen free atmosphere. During carbonization the hydrogen, nitrogen and oxygen atoms are removed from the polymer chains

leading to formation of pure carbon nanofibers with decreased diameter[8]. Higher carbonization temperature leads to higher graphitization of the fibers and therefore enhanced conductivity and mechanical properties[20].

As mentioned, the stabilization step has a vital effect not only on the conditions and success of the carbonization step, but also on the properties of the final carbon nanofiber products. However, very few studies are concentrated on the effect the stabilization conditions on the morphology and chemical state of the stabilized PAN. Most studies in the literature use high molecular weight precursors. Only a handful of researchers have focused on the stabilization step of electrospun PAN nano-fibers. In this study, a low molecular weight PAN was used for the first time. In addition, this low molecular weight PAN was obtained locally from Iranian sources which paves the way for future low-cost mass production of carbon nano-fibers. In the present study, the effect of stabilization temperature has been studied on the morphology and chemical state of electrospun PAN fibers synthesized from low molecular weight PAN precursors. Also, a relatively low carbonizing temperature was chosen due to the low molecular weight of the precursor and other conditions were based on previous investigations.

2. Experimental method

2.1. Materials

Polyacrylonitrile (PAN) with an average molecular weight (MW) of 75000 g/mol (Polyacryl Iran) and N,N-dimethylformamide (DMF) solvent with purity of 99.5%, molecular mass 73.09 g/mol and liquid form (Merck, Germany) were used to prepare the electrospinning solutions.

2.2. Nanofiber production

In the first step, 1.5 g of PAN was slowly added to 10 ml of DMF and stirred for 2 hours at room temperature to achieve a homogenous and clear solution. Electrospinning was performed for 2 hours on a lab-scale electrospinning machine (Fanavaran Nano-Meghyas, Iran). The rotational speed of the collector drum was set to 1000 rpm, the nozzle to collector drum distance was set at 15 cm and electrospinning was carried out under the voltage of 15 kV with a solution flow rate of 1 ml/h.

The electrospun PAN fibers were stabilized in an oven at different temperatures of 280 °C, 250 °C, 240 °C and 230 °C for 2 hours with a heating rate of

2 °C/min. It is worth mentioning that stabilization temperatures below 230 °C did not show any significant changes in the FTIR spectra of the PAN fibers; therefore, the lowest studied temperature was set at 230 °C. Finally, carbonizing was carried out in a tubular furnace at 650 °C for 2 hours with a heating rate of 5 °C/min under nitrogen atmosphere.

2.3. Characterization

The morphology of the as-electrospun, stabilized and carbonized fibers were investigated using a scanning electron microscope (SEM - LEO, VP 1450). The chemical state of the PAN fibers before and after stabilization, as well as the resulting CNF was investigated using Fourier transform infrared spectrometer (FTIR - Thermo Nicolet, AVATAR 370 FT-IR). The crystal structure of the as electrospun PAN fibers before and after stabilization at different temperatures and after carbonization was studied using X-Ray diffraction (XRD Exprorer- GNR Italy) method with a Cu Ka radiation and 2θ between 5 and 80°.

3. Results and Discussion

In the first step, the color of the electrospun fibers before and after stabilization at different temperatures as well as after carbonization was

investigated. Figure 1 shows photographs of (A) as electrospun PAN fibers, along with stabilized fibers at different temperatures of (B) 230 °C, (C) 240 °C, (D) 250 °C and (E) 280 °C, respectively and (F) the carbonized fibers. According to these images, the as electrospun PAN fibers had a white color which is expected due to the natural color of PAN Figure 1(A) After stabilization at 230 °C and 240 °C the color changed to light brown and by increasing the stabilization temperature, darker colors were observed. At 250 °C, the sample was brown and the sample stabilized at 280 °C was dark brown. Differences in samples colors at different temperatures are the result of more progress in reactions during stabilization, however it should be noted that higher temperatures may result in fibers melt down or decomposition. As observed in Figure 1(F), the carbonized sample was black indicating that carbonization was completed.

During the stabilization process, the chemical structure of PAN fibers and their bonds change. Cyclization, dehydrogenation, oxidation and cross-linking are the four major reactions that happen during stabilization process. These reactions are schematically shown in Figure 2 During cyclization, linear C≡N bands are replaced by C=N in Benzene rings, which as a result lead to an increase in the density and tensile strength of PAN[10,21,22].



Fig. 1- photograph of: (A): as-electrospun and stabilized fibers at (B) 230 °C, (C) 240 °C, (D) 250 °C, (E) 280 °C and (F) CNF.

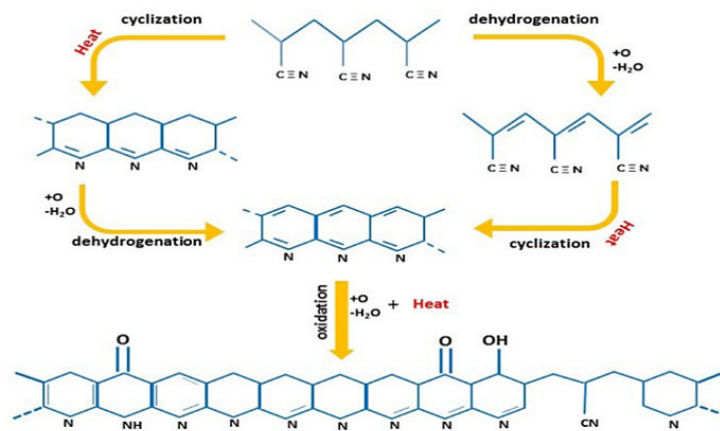


Fig. 2- Stabilization reactions for PAN nano-fibers.

The dehydrogenation reaction leads to a decrease in C-H bonds and hydrogen leaves the structure in the form of H₂O. In the oxidation reaction, which is an exothermic reaction, some oxygen containing groups are added to the structure. Proper selection of the stabilization temperature, time and heating rate, plays an important role in the progress of the aforementioned reactions. A very low temperature might lead to incomplete reactions while a too high one results in melting or decomposing of the PAN fibers. Furthermore with a low heating rate, cross-linking occurs before releasing tension and by decreasing permeability of fibers, the structure will be preserved[22, 23].

Finally, in carbonizing process, nitrogen and hydrogen are removed from the structure and the resultant fibers should consists of about 98% carbon. In order to track these changes during stabilization and carbonization process, as well as finding the optimum stabilization temperature, FTIR was employed.

Figure 3(A) shows the FTIR spectra of the electrospun pan fibers before and after stabilization at different temperatures as well as after carbonization. According to the FTIR spectra, the as-electrospun PAN fibers consist of characteristic vibration peaks at 2243 cm⁻¹, 2931 cm⁻¹ and 1420 cm⁻¹ corresponding to C≡N, ν-CH₂ and σ-CH₂ groups respectively. Stabilization was carried out at different temperatures of 230, 240, 250 and 280 °C. After stabilization at all temperatures, a drastic drop is observed in the intensity of the vibration peaks at 2243, 2931 and 1420 cm⁻¹, indicating the progress of cyclization and dehydrogenation reactions[19].

Figure 3(A) shows the FTIR spectra of the

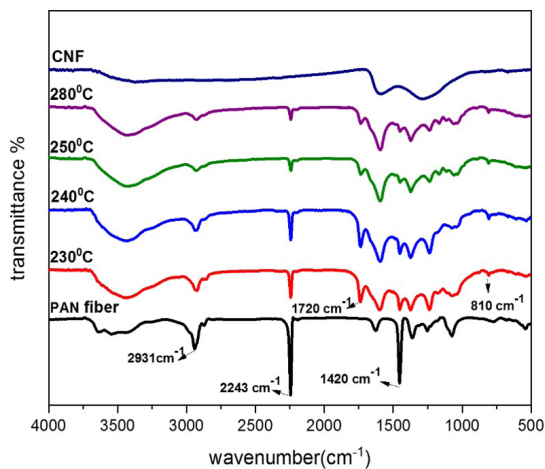


Fig. 3- FTIR spectras of PAN fiber, stabilized samples at different temperature and CNF.

electrospun pan fibers before and after stabilization at different temperatures as well as after carbonization. According to the FTIR spectra, the as-electrospun PAN fibers consist of characteristic vibration peaks at 2243 cm⁻¹, 2931 cm⁻¹ and 1420 cm⁻¹ corresponding to C≡N, ν-CH₂ and σ-CH₂ groups respectively. Stabilization was carried out at different temperatures of 230, 240, 250 and 280 °C. After stabilization at all temperatures, a drastic drop is observed in the intensity of the vibration peaks at 2243, 2931 and 1420 cm⁻¹, indicating the progress of cyclization and dehydrogenation reactions[24]. On the other hand, the intensity of some peaks between 1400-1600 cm⁻¹ has increased after stabilization. These peaks are related to C=N, C-N and C=C bands. Besides, the peak observed at 1720 cm⁻¹ shows the existence of oxygen containing groups in the stabilized fibers, developed during the oxidation[24,25,26]. Another new peak observed at 810 cm⁻¹ is related to C=C-H in the stabilized PAN fibers[24].

Comparing the FTIR spectra of the stabilized PAN fibers at different temperatures, it is observed that, higher stabilization temperatures lead to more decrease in the intensity of the peaks at 2243 cm⁻¹, 2931 cm⁻¹ and 1420 cm⁻¹ indicating more progress of reactions at higher temperatures. Also according to the FTIR spectra, expected no reactions do as well at the temperature below 230 °C. Finally the FTIR spectrum of the carbonized fibers displays two characteristic peaks at 1600 cm⁻¹ and 1290 cm⁻¹ corresponding to C=C Bonds in Carbon nanofibers.

Figure 4 shows the XRD patterns of the as electrospun, stabilized and carbonized PAN fibers. Two peaks are observed in the XRD pattern of the

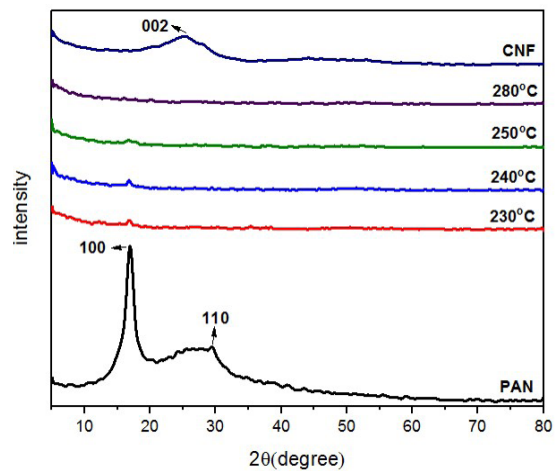


Fig. 4- XRD pattern of PAN fiber, stabilized fiber and CNF.

as-electrospun PAN fibers, at $2\theta = 16.71^\circ$ and $2\theta = 29.36^\circ$ which correspond to the (100) and (110) planes, respectively. XRD results after stabilization show that the intensity of the (100) peak is greatly decreased after stabilization at 230, 240 and 250 °C. Moreover, higher stabilization temperature leads more decrease in the intensity of this peak and it almost disappeared at 280 °C. Besides, it is observed that the peak corresponding to (110) crystallographic plane of PAN is disappeared after stabilization at all temperatures. The changes of these peaks were due to the changes of the PAN crystallographic structure during the stabilization process, which is mainly a result of the cyclization and dehydrogenation reactions.

In cyclization reaction, by replacing of the $C\equiv N$ bonds with $C=N$ and formation of the ladder/ring structure, the orientation of chains destroyed and crystallinity decreased.

The excess nitrogen & hydrogen atoms present in the stabilized PAN fibers must be removed during the carbonization step in order to produce pure carbon fibers. The carbonization temperature mainly depends on the molecular weight of the precursor, stabilization temperature and the desired crystallinity of the product. The carbonization temperature was therefore chosen accordingly based on previous published work[27]. After carbonization, only one peak is observed at $2\theta = 25.67^\circ$ which is the characteristic peak of the

(002) crystallographic plan of graphitic structure, suggesting successful carbonization of the fibers and achievement of carbon nanofibers.

Figure 5 shows SEM images of the as electrospun PAN fibers along with stabilized and carbonized samples. As shown in Figure 5(A), electrospun PAN fibers have a perfect smooth and bead-free morphology showing the successful electrospinning process. Figure 5(B and C) show stabilized samples at 250°C and 280°C respectively. High temperature and diffusion during the stabilization resulted in surface melting and welding (re-bonding) of the fibers together, they had no fiber structure. It shows that the stabilized temperatures were high and it has damaged the fiber structure. Figure 5(D and E) show the stabilized samples at 240 °C and 230 °C. According to these images, no surface melting is observed and the fiber structure is well preserved after stabilization at 230 °C and 240 °C.

These two samples show little shrinkage in structure, which is due to the limited weight reduction of fibers during of stabilization[24]. Considering the slight sticking of the fibers at 240 °C, it is concluded that the 230 °C is an optimum stabilization temperature to preserve the fiber structure. Carbonized sample had the same structure as the stabilized sample at 230 °C; the only difference was that its fibers were finer (Figure 4F). The average diameter of electrospinning sample equals to 350 nm that shows no significant change

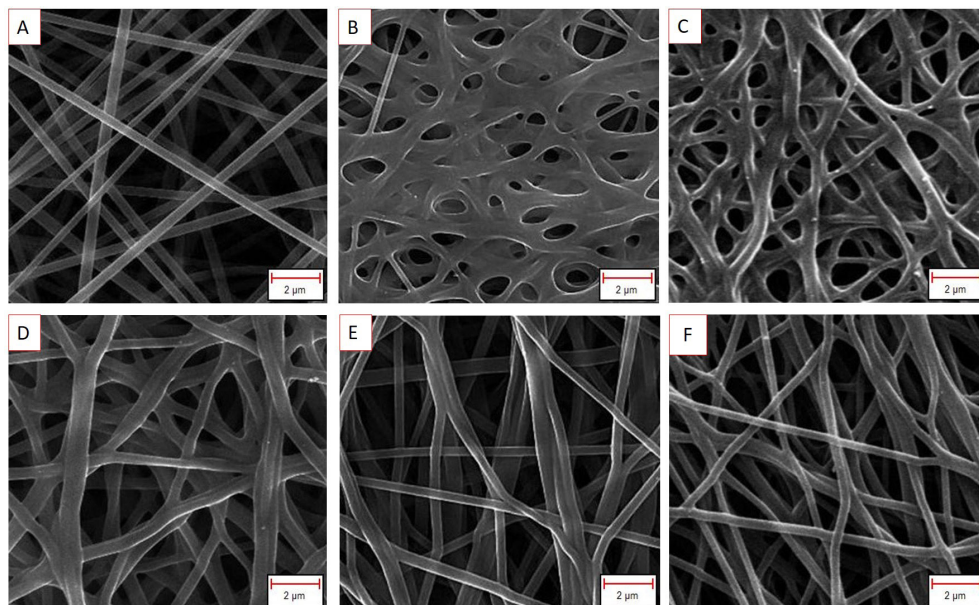


Fig. 6- SEM image of samples: (A): PAN fibers, (B): stabilized at 230 °C, (C): stabilized at 240 °C, (D): stabilized at 250 °C, (E): stabilized at 280 °C and (F): CNF.

during stabilization. In carbonization process, oxygen and nitrogen left the structure and the diameter of fiber decreased. The average diameter of fibers in CNF was equal to 190 nm.

4. Conclusions

PAN fibers were produced by electrospinning the PAN/DMF solution. Then stabilization was carried out on electrospun fibers at different temperatures of 230, 240, 250 and 280 °C. XRD, FTIR and SEM were used to study the crystallinity, chemical state and morphology of the fibers. According to the XRD results, the intensity of peaks related to (100) and (110) crystallographic plans of PAN, decreased drastically after stabilization at all temperatures, showing the change in the crystalline structure of PAN fibers after stabilization. FTIR studies showed that with increasing the stabilization temperature, the intensity of the characteristic vibration peaks of PAN at 2243 cm^{-1} , 2931 cm^{-1} and 1420 cm^{-1} corresponding to the $\text{C}\equiv\text{N}$, $\nu\text{-CH}_2$ and $\sigma\text{-CH}_2$ groups respectively, saw a drastic drop after stabilization at all temperatures and in return new peaks emerged at 810 cm^{-1} corresponding to $\text{C}=\text{C-H}$ groups, 1720 cm^{-1} corresponding to oxygen containing groups. Furthermore the intensity of the peaks between 1400-1600 cm^{-1} related to $\text{C}=\text{N}$, C-N and $\text{C}=\text{C}$ bands increased after stabilization. Besides, increasing the stabilization temperature resulted in higher degree of change in the aforementioned peaks. These changes prove the progress of the cyclization, dehydrogenation, cross linking and oxidation reactions. On the other hand, SEM studies showed that by increasing the stabilization temperature from 230 to 280 °C, the fibers start to meld and re-weld to each other leading to destruction of the morphology. The best morphology was achieved at 230 °C, which regarding the XRD and FTIR results, it is postulated to be the optimum stabilization temperature for PAN (MW 75000) fibers. Finally carbonization was carried out on the optimum stabilized fibers and pure carbon nanofibers were achieved.

References

- Jalili R, Morshed M, Ravandi SAH. Fundamental parameters affecting electrospinning of PAN nanofibers as uniaxially aligned fibers. *Journal of Applied Polymer Science*. 2006;101(6):4350-7.
- Dhakate SR, Gupta A, Chaudhari A, Tawale J, Mathur RB. Morphology and thermal properties of PAN copolymer based electrospun nanofibers. *Synthetic Metals*. 2011;161(5-6):411-9.
- Thompson CJ, Chase GG, Yarin AL, Reneker DH. Effects of parameters on nanofiber diameter determined from electrospinning model. *Polymer*. 2007;48(23):6913-22.
- Qin X-H. Structure and property of electrospinning PAN nanofibers by different preoxidation temperature. *Journal of Thermal Analysis and Calorimetry*. 2009;99(2):571-5.
- Gu SY, Ren J, Wu QL. Preparation and structures of electrospun PAN nanofibers as a precursor of carbon nanofibers. *Synthetic Metals*. 2005;155(1):157-61.
- Begum HA, Khan KR. Study on the various types of needle based and needleless electrospinning system for nanofiber production. *Int. J. Text. Sci.* 2017;6:110-7.
- Zhang B, Kang F, Tarascon J-M, Kim J-K. Recent advances in electrospun carbon nanofibers and their application in electrochemical energy storage. *Progress in Materials Science*. 2016;76:319-80.
- Feng L, Xie N, Zhong J. Carbon Nanofibers and Their Composites: A Review of Synthesizing, Properties and Applications. *Materials (Basel)*. 2014;7(5):3919-45.
- Kil H-S, Jang SY, Ko S, Jeon YP, Kim H-C, Joh H-I, et al. Effects of stabilization variables on mechanical properties of isotropic pitch based carbon fibers. *Journal of Industrial and Engineering Chemistry*. 2018;58:349-56.
- Rahaman MSA, Ismail AF, Mustafa A. A review of heat treatment on polyacrylonitrile fiber. *Polymer Degradation and Stability*. 2007;92(8):1421-32.
- Yamane A, Sawai D, Kameda T, Kanamoto T, Ito M, Porter RS. Development of High Ductility and Tensile Properties upon Two-Stage Draw of Ultrahigh Molecular Weight Poly(acrylonitrile). *Macromolecules*. 1997;30(14):4170-8.
- Liu J, Zhou P, Zhang L, Ma Z, Liang J, Fong H. Thermochemical reactions occurring during the oxidative stabilization of electrospun polyacrylonitrile precursor nanofibers and the resulting structural conversions. *Carbon*. 2009;47(4):1087-95.
- Zhang P, Shao C, Zhang Z, Zhang M, Mu J, Guo Z, et al. In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol. *Nanoscale*. 2011;3(8):3357.
- Sun G, Sun L, Xie H, Liu J. Electrospinning of Nanofibers for Energy Applications. *Nanomaterials (Basel)*. 2016;6(7):129.
- Shi X, Zhou W, Ma D, Ma Q, Bridges D, Ma Y, et al. Electrospinning of Nanofibers and Their Applications for Energy Devices. *Journal of Nanomaterials*. 2015;2015:1-20.
- Faccini M, Borja G, Boerrigter M, Morillo Martín D, Martínez Crespiera S, Vázquez-Campos S, et al. Electrospun Carbon Nanofiber Membranes for Filtration of Nanoparticles from Water. *Journal of Nanomaterials*. 2015;2015:1-9.
- Mao X, Simeon F, Rutledge GC, Hatton TA. Electrospun Carbon Nanofiber Webs with Controlled Density of States for Sensor Applications. *Advanced Materials*. 2012;25(9):1309-14.
- Hong X, Chung DDL. Carbon nanofiber mats for electromagnetic interference shielding. *Carbon*. 2017;111:529-37.
- Zhou Z, Lai C, Zhang L, Qian Y, Hou H, Reneker DH, et al. Development of carbon nanofibers from aligned electrospun polyacrylonitrile nanofiber bundles and characterization of their microstructural, electrical, and mechanical properties. *Polymer*. 2009;50(13):2999-3006.
- Alarifi IM, Khan WS, Asmatulu R. Synthesis of electrospun polyacrylonitrile- derived carbon fibers and comparison of properties with bulk form. *PLoS One*. 2018;13(8):e0201345-e.
- Fitzer E, Frohs W, Heine M. Optimization of stabilization and carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibres. *Carbon*. 1986;24(4):387-95.
- Nie G, Zhao X, Luan Y, Jiang J, Kou Z, Wang J. Key issues facing electrospun carbon nanofibers in energy applications: on-going approaches and challenges. *Nanoscale*. 2020;12(25):13225-48.
- Yusof N, Ismail AF, Jaafar J, Salleh WNW, Hasbullah H.

- Effects of Stabilization Temperature on the Chemical and the Physical Properties of Polyacrylonitrile Stabilized Fibers. *Advanced Materials Research*. 2015;1112:402-5.
24. Wu M, Wang Q, Li K, Wu Y, Liu H. Optimization of stabilization conditions for electrospun polyacrylonitrile nanofibers. *Polymer Degradation and Stability*. 2012;97(8):1511-9.
25. Esrafilzadeh D, Morshed M, Tavanai H. An investigation on the stabilization of special polyacrylonitrile nanofibers as carbon or activated carbon nanofiber precursor. *Synthetic Metals*. 2009;159(3-4):267-72.
26. Duan Q, Wang B, Wang H. Effects of Stabilization Temperature on Structures and Properties of Polyacrylonitrile (PAN)-Based Stabilized Electrospun Nanofiber Mats. *Journal of Macromolecular Science, Part B*. 2012;51(12):2428-37.
27. Abouali S, Akbari Garakani M, Zhang B, Xu Z-L, Kamali Heidari E, Huang J-q, et al. Electrospun Carbon Nanofibers with in Situ Encapsulated Co₃O₄ Nanoparticles as Electrodes for High-Performance Supercapacitors. *ACS Applied Materials & Interfaces*. 2015;7(24):13503-11.