

# Development of Carbon Nanofiber Yarns by Electrospinning

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**Abstract.** In recent years the commercial importance of carbon nanofiber has increased due to its high mechanical properties, electrical and thermal conductivity and lightness. Therefore, carbon nanofibers are candidate to replace many commercial products. In general carbon nanofibers are produced from precursor fiber. Polyacrylonitrile (PAN) is usually used as precursor fiber because of comparatively high carbon yield and a thermally stable and highly oriented molecular structure. Large number of scientific publications have been demonstrated with the help of progress in nanofiber production methods, such electrospinning, centrifugal-spinning, air blowing from melt or solution, and optimization of process parameters of those methods. In this study, PAN nanoyarn is first obtained by the electrospinning method which is very convenient process for producing thin fiber. Stabilization is then applied by exposure to air at 230°C to provide thermally stable structure so that the resulting PAN nanofibers could be thermally durable during the carbonization process at high temperature. Finally, the process for the carbonization of the stabilized sample is operated in a argon gas atmosphere at 600°C. The produced material is characterized by SEM to observe its morphology.

## 1. Introduction

Production of nanofibers from polymer materials has been a very important part of the nanotechnology, which is the most important area of scientific and technological activities in the last 10 years. Large number of scientific publications has been published with the help of progress in nanofibre production methods, such as electrospinning, centrifugal-spinning, air blowing from melt or solution, and optimization of process parameters of those methods.

Nanofibers use of many areas such as composite applications, filtration membranes, biomedical materials and tissue engineering because of high area and good strength properties provided by unit weight. Despite all this, in the electrospinning method, randomly oriented nanofibers are produced which limit the application area of the final product. Thus many researchers have recently started to work on nanofiber yarn production. Because the nanofiber yarns have higher mechanical strength than the randomly positioned nanofiber webs, in order to produce nanofiber yarns, researchers have improved many novel electrospinning techniques. One of these is the double electrode disc twisting device which was developed by Ali et al. [1]. In this method, an earthed funnel collector, two opposite charged nozzles and a take up roller were used and the nanofibers formed from the opposite charged nozzles became nanofiber yarn in the middle. In recent studies, it seems that double needle disc twisting yarn device is commonly used for preparing twisted nanofiber yarns. This device was





modified using multiple-needle by He et al. [2]. In this work, there was just a difference that was the number of the needles. He et al., used two opposite charged infusion tubes which have four needles in each tube. It resulted in increased nanofiber production therefore more nanofiber yarn formation. On the other hand, in recent years, activated carbon fibers have been widely used in textiles, air filters, supercapacitors, wound dressings and insulation materials due to their high porosity, high adsorption ability, excellent electrochemical properties and flexibility, therefore carbon nanofiber yarns have become the focus of researchers. Carbon nanofiber are obtained by carbonization after the stabilization processes. In generally, carbonization is carried out in argon or nitrogen atmosphere at high temperature and stabilization takes place in air atmosphere at high temperature. Moon and Farris studied on the electrospun PAN carbon fiber yarns [3], they formed good aligned nanofiber yarn via electrospinning method and the produced twisted PAN nanofiber yarn is stabilized in air at a specific high temperature and then carbonized at high temperature in a nitrogen atmosphere. The mechanical strength of carbonized and untreated PAN nanofiber yarns was evaluated and as expected the carbon nanofiber yarn had high mechanical strength because of the conversion to a stable and strong cross-linked structure from a ladder structure. Another study on this subject was made by Chawla et al. [4]. They examined the conductivity of nanofiber yarns which was affected the level of twisting. In this work, the PAN nanofiber yarns obtained via electrospinning technique and they were then stabilized at 250°C in air in an oven for 1 hour. After stabilization, the nanofiber yarns were carbonized in a tube furnace at 1100°C for 1 hour in a nitrogen atmosphere. According to the results of this study, the level of twisting enhanced the molecular orientation and increased the alignment of nanofiber yarns. However the further increment of this level gave rise to fiber breakage and conductivity drop. It is possible to increase the properties of the fiber by carbonization, for example the conductivity of the material. Works on the conductivity properties of carbon nanofibers have increased with reasons such as carbonization of the material becoming similar to the graphitic structure, reduction of the diameter and increase of the strength. The carbonization temperature affects the properties of the ultimate product. Panapoy M. et al. [5] showed that increasing carbonization temperature increases the conductivity of the material. By carbonization, the nitrogen groups disappear so that the structure of the fiber is similar to the graphite structure with high carbon content. The increase in the graphite structure due to the high temperature causes the resonance vibration effect of the  $\pi$  bond in the graphite structure and it leads to the electrons in the carbon layer to move. As a result, the electrical conductivity increases.

Thanks to the superior properties of the carbon nanofiber yarns in each application area, the study for the use of carbon nanofiber yarns has increased day by day. In this context, in this work we aimed to produce the PAN nanofiber yarn via electrospinning method and to improve the properties of PAN nanofiber yarn by carbonization in argon atmosphere at high temperature.

## 2. Experimental

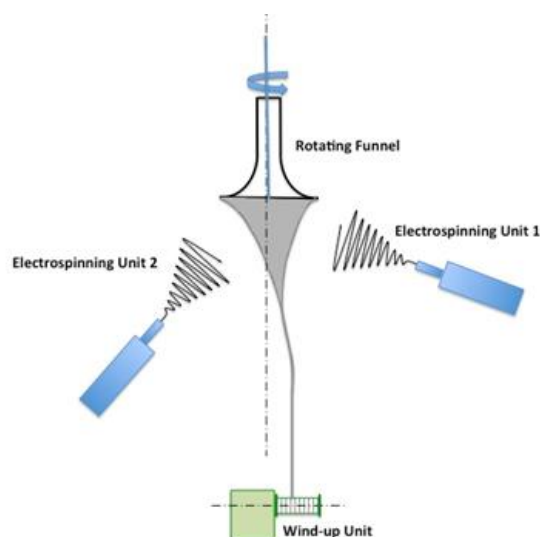
### 2.1. Materials

The polymer used was polyacrylonitrile (PAN) and the solvent used was N,N-dimethylformamide (DMF). The 8% electrospinning solution was prepared by dissolving the required amounts of polymers in the solvents at the required temperature.

### 2.2. Electrospinning of nanofiber yarn

Nanofiber yarn electrospinning system consists of three needle nozzles placed on a circular path 120° apart from each other, a purpose-designed cylindrical collector, a high-voltage power supply and yarn winding system (Figure 1 represents a schematic view of the system). The collector was encircled by three spinnerets, and winding system was placed underneath the rotating collector.





**Figure 1.** Schematic view of nanofiber yarn production system

All three spinnerets were connected to 20 kV positive high power supply. Electrospun nanofibers were deposited onto the rotating cylinder collector and formed a nanofiber web that covers the end of the collector. Nanofiber yarn was drawn by the help of a conventional guide yarn which was loosely attached to the collector.

### 2.3. Stabilization and carbonization of nanofiber yarn

The produced PAN nanofiber yarn was wrapped on a glass rod (Figure 2) then it was stabilized at 230°C under air with a heating rate of 1°C/min before carbonization to provide thermal stability. The stabilized nanofiber yarn (SNFY) was then carbonized. The sample was carbonized by three stage heating in argon gas to avoid degradation of the sample with rapid temperature rise. In the first step, the sample was heated to 50°C (heating rate: 1°C/min), after that the temperature reached to 300°C at a heating rate of 0.5°C/min. In the last step the temperature came up to 600°C with a heating rate of 3°C/min and it was left at this temperature for 30 min.



**Figure 2.** The PAN nanofiber yarn before stabilization

### 2.4. Characterization

The PAN nanofiber yarn, SNFY and carbonized nanofiber yarn (CNFY) were examined by SEM analysis. The morphology and diameter of these samples were observed from the SEM images.

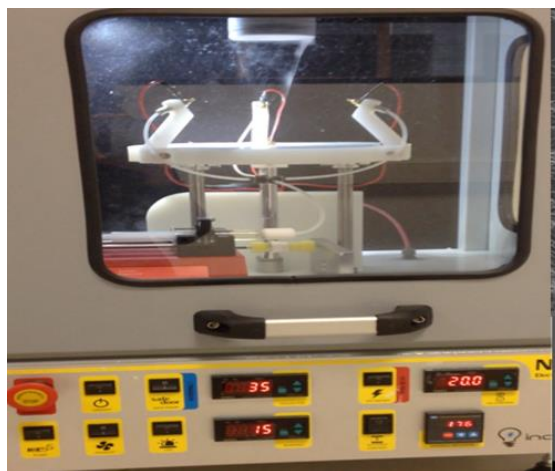
## 3. Results

### 3.1. Nanofiber yarn

Nanofiber yarn was electrospun continuously by using the Inovenso NanoYarn machine as shown in the Figure 3, from 8% PAN solution. Optimized results were obtained by 1,5 ml/h feeding rate, 20 kV



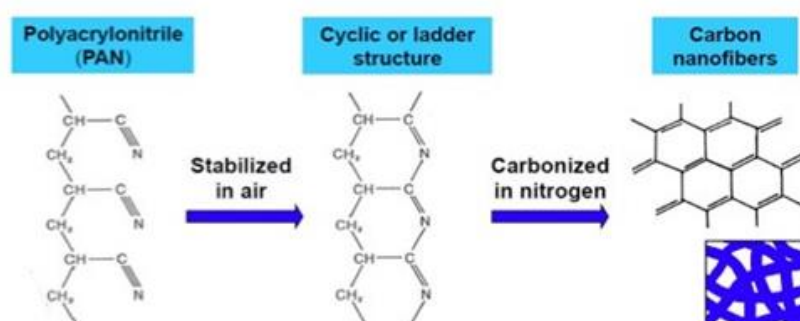
voltage and 350 rpm rotation speed of the collector. Nanofibers were electrospun from positively charged three spinnerets and deposited onto the grounded rotating cylindrical collector. Nanofibers were mainly deposited onto the mouth end of the collector due to the structure of the collector. A conventional yarn was used as a guide to draw nanofiber yarn from collector to the winding system. Some of the deposited nanofibers were joined to the cone shaped web formation and some of them were also deposited at the inner edges of the collector. The reason could be electrostatic interaction between positively charged nanofibers. They are in tendency of repelling each other and depositing on grounded collector.



**Figure 3.** Nanofiber yarn obtained by the Inovenso NanoYarn device using 8% PAN solution

### 3.2. Stabilized and carbonized nanofiber yarns

As it can be seen in Figure 4, during the stabilization the macromolecular chain of PAN turns into ladder type structure due to the chemical reactions such as oxidation, dehydrogenation and cyclization and a result of  $C\equiv N$  bonds convert to  $C=N$  and finally to  $C-N$  bonds [6]. Therewithal the colour of the sample turns dark brown and the weight of sample and fiber diameter decrease due to the removing of  $CN$  and  $CH_2$  groups from the sample. The temperature effects the reaction rates of stabilization process therefore the temperature should be optimum level. If the temperature is low, the reaction takes place with slow kinetic or it may not become true. On the other hand the high temperature leads to degradation of the sample and loss of molecular orientation. In the Figure 5, the SNFY and CNFY are shown.

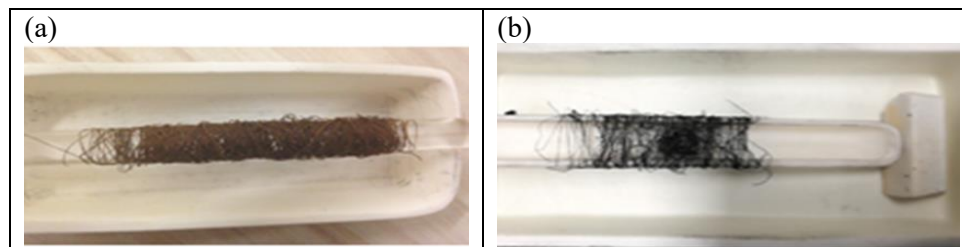


**Figure 4.** Steps of preparation of carbon nanofibers

During the carbonization process some non-carbon elements such as hydrogen, nitrogen, oxygen and sulfur are eliminated from fibers. As a result shrinkage occurs in the fibers and the diameter

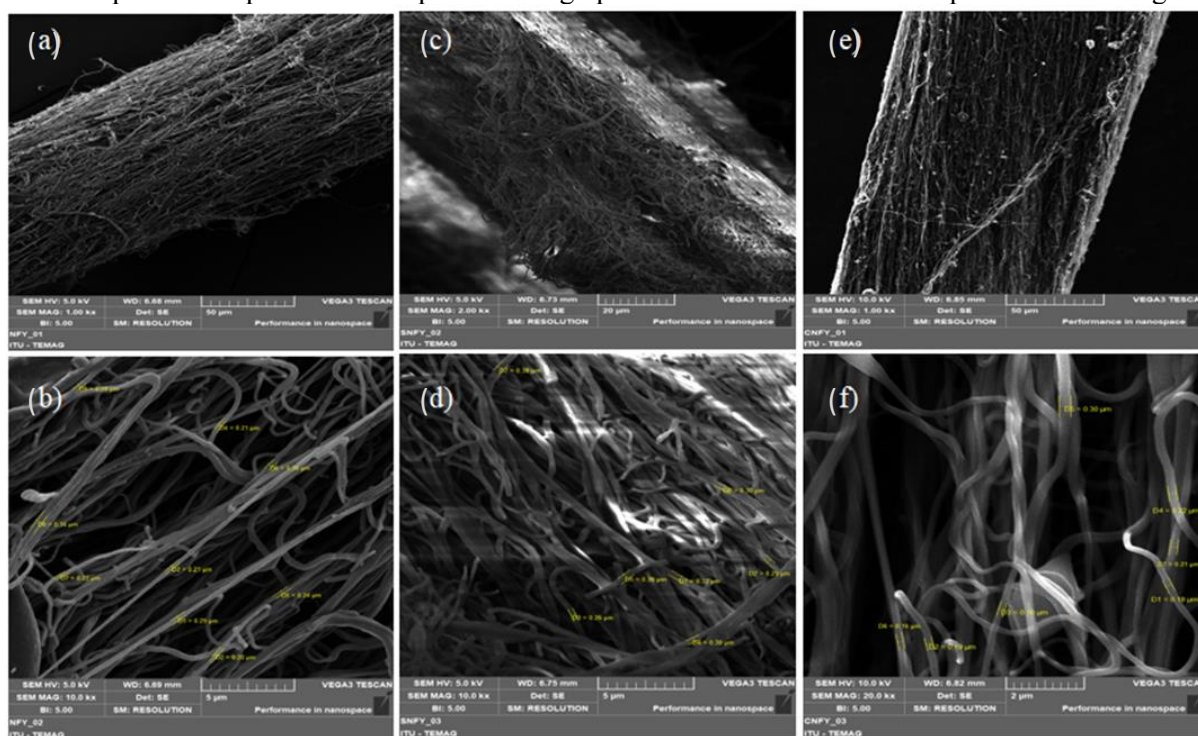


decreases. Carbonization process causes the nitrile groups to disappear and that indicates cyclization of the structure like graphite fiber [7].



**Figure 5.** (a) Stabilized PAN nanofiber yarn and (b) Carbonized PAN nanofiber yarn

As seen in Figure 6, continuity of yarn was maintained after the carbonization and the diameter of fibers also decreased. The range of the diameter of the untreated PAN nanofiber yarn was between 210 nm and 340 nm while CNFY had a diameter between 160 nm and 300 nm. Carbonization temperature is important parameter for ultimate material properties. If they are low, the removal of nitrogen groups can not be achieved and carbon nanofiber yarn can not be produced in the desired yield. On the other hand it is possible to perform a complete burning operation in the case that these parameters are high.



**Figure 6.** SEM images of (a) PAN nanofiber yarn with 1.00kx (b) PAN nanofiber yarn with 10.0kx (c) stabilized PAN nanofiber yarn with 1.00kx (d) stabilized PAN nanofiber yarn with 10.0kx (e) carbonized PAN nanofiber yarn with 1.00kx and (f) carbonized PAN nanofiber yarn with 20.0kx

#### 4. Conclusion

The experimental work has successfully shown that PAN based carbon nanofiber yarn could be achieved. It has been discussed that PAN/DMF solutions prepared by low molecular weight PAN could not be carbonised due to the lack of required intramolecular forces. However, as the molecular weight of the PAN exceeds 150 000 g/mol, both stabilization as well as the carbonization stages of the conversion could be easily managed.



Having achieved carbon nanofiber yarns by utilising the electrospinning-stabilization-carbonization process chain in a multi step operation, it is now our intention to design and develop an on-line process to achieve all these three steps sequentially or if possible simultaneously.

### Acknowledgments

This work has been carried out by the Research and Development grant by TUBITAK and INOVENSO with the R&D Project Number 0937.STZ.2015.

### References

- [1] Ali U, Zhou Y, Wang X and Lin T 2012 Direct electrospinning of highly twisted, continuous nanofiber yarns *The journal of the textile institute* **103** 80-88
- [2] He J, Qi K, Zhou Y and Cui S 2014 Multiple conjugate electrospinning method for the preparation of continuous polyacrylonitrile nanofiber yarn, *Journal of applied polymer science* **131** 40137
- [3] Moon S C and Farris R J 2009 Strong electrospun nanometer-diameter polyacrylonitrile carbon fiber yarns *Carbon* **47** 2829-2839
- [4] Chawla S, Naraghi M and Davoudi A 2013 Effect of twist and porosity on the electrical conductivity of carbon nanofiber yarns *Nanotechnology* **24** 255708
- [5] Panapoy M, Dankeaw A and Ksapabutr B 2008 Electrical conductivity of PAN-based carbon nanofibers prepared by elektrospinning method, *Thammasat international journal of science and technology* **13** special edition 11-17
- [6] Esrafilzadeh D, Morshed M and Tavanai H 2009 An investigation on the stabilization of special polyacrylonitrile nanofibers as carbon or activated carbon nanofiber precursor *Synthetic metals* **159** 267-272.
- [7] Su C I, Huang Y X, Wong J W, Lu C H and Wang C M 2012 PAN-based carbon nanofiber adsorbents prepared using elektrospinning *Fibers and polymers* **13** 436-442