REVIEW ON CREATION OF CARBON NANOFIBERS

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Abstract

PAN nanofibers can be easily converted into carbon nanofibers. Nanofibers are used in various applications due to their physical and chemical properties. Carbon nanofibers are made by carbonization process. Carbonization is done in an inert environment at high heat. However the heat required to carbonize the fibers usually destroy the fibers. To avoid this condition stabilization process is done. Stabilization is process of heating fibers in air. This process provides a ladder like structure to fiber. This process consumes considerable amount time and energy which add additional cost for making carbon nanofibers.

Keywords: Nanomaterials, Electrospinning and Carbon nanofibers

Introduction

Nanotechnology is very innovative field finding various applications in biomedical, Mechanical, Automobile, electronics and electrical industries. Nanomaterials have grain size between 1 to 100nm [1].Nanomaterials has different types of dimensions zero, one, two and three dimension. According this dimension there are different types of materials such as spheres cluster (0D), nanofibers, wires and rod (1D), films, plates and networks (2D), nanomaterials (3D).

Carbon nanofibers are mostly used nanomaterials because of its different properties and potentials application. They are unique for their large surface area-to-volume ration, mechanical strength, and flexibility. For generating carbon nanofibers chemical precursor required of high-quality carbon fibers. Polyacrylonitrile (PAN) has high quantity of carbon, PAN made from mixtures of monomers with acrylonitrile as the main component. There are different types of synthesis methods such as Drawing, Template Synthesis, Phase Separation, Self-Assembly, Melt-blown technology and Electrospinning for making nanofibers, but Electrospinning technics had mostly used [2].

Electrospinning is a very simple and very cost effective technique is used to produce nanofibers, in this process polymer solution of PAN used for making nanofibers, this solution of polymers gets converted into nanofibers using very high electric field [3-4]. When electric field is applied to solution at the tip of the syringe small droplet forms, when an electric field is increased droplet of solution transforms in to cone shape this is called Taylor cone as shown in Fig.1 and further increasing high voltage fibers will ejected and collect to collector drum [5-6].

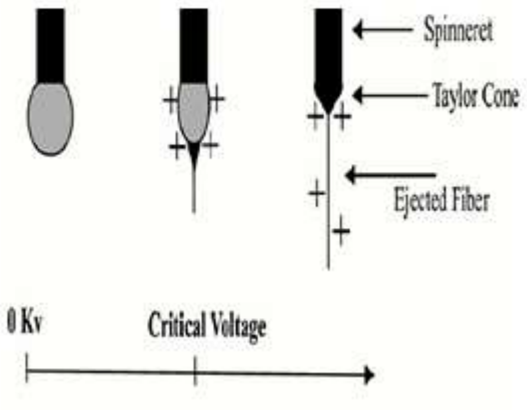

fig. 1 increasing applied voltage [3].

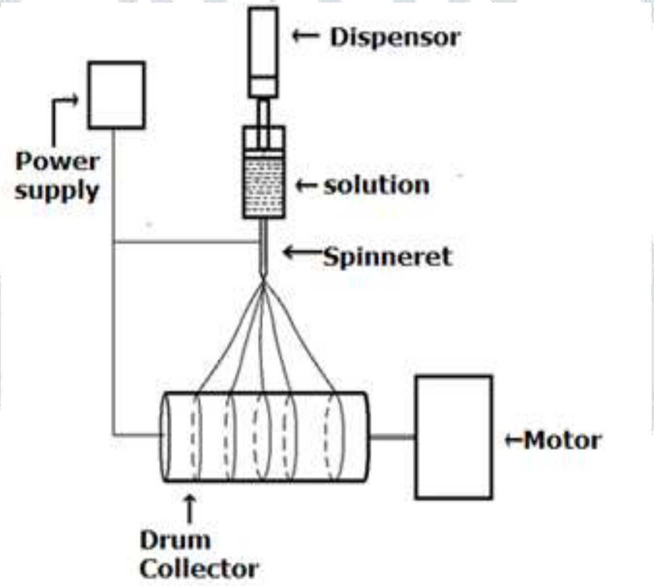

fig.2 schematic diagrams of manufacturing of electrospun nanofibers [3].

We studied PAN nanofibers production by using different parameters. Later PAN nanofibers were heated at 1000 to 2000 ^{0}C to recreate carbon nanofibers.

Vahid Mottaghitalab and Akbar Khodaparast Haghi [7] evaluated electrospinning of PAN nanofibers. The fibers manufactured were well-aligned polymer nanofibers having concentration of PAN solution from 10% to 15%. Distance from tip of syringe to drum was 15cm, 20KV applied voltage, 1.5mL/h flow rate this parameter had used to getting nanofibers. After studied this experiment they conclude that size of the fibers was increased with increasing concentration of the PAN in solution means diameter of fibers was increased with high concentration of PAN and they also studied the molecular orientation of nanofibers which make effect on the mechanical properties of nanofibers.

Yu-Qin Wan, Ji-Huan He *el al.* [8] studied CNTs as reinforced in PAN for enhancing material for composites using traditional electrospinning and vibration electrospinning process for manufacturing nanofibers. The concentration of PAN/DMF solution was 18% and this solution was stirring for 1h at 70^0 C. After cooling in room temperature MWCNTs (2%) added into PAN solution and then again stirred for 1h, then this solution used for making nanofibers. In result they got average diameter of about 100nm and the surface of PAN fibers was smooth and PAN fibers were successfully filled with MWCNTs.

S.K. Nataraja, K.S. Yang *et al.* [6] discussed that PAN-based CNFs are seemingly a new class of materials used in a wide array of applications including filtration barriers, material reinforcements, garments, insulators, medical and energy storage devices, and many more. However, their unique properties make them perfect modern materials of choice across many disciplines covering engineering, medicine, and biology. The accelerating technologies of producing PAN-based nanofibers have now matured enough to overcome the drawbacks of low production rate of few grams per hour in laboratory environments to large industrial scale production. Nanofiber membranes comprising sheets of randomly oriented nanofibers show an extremely effective removal method with a high rejection rate of airborne particles by both physical trapping and adsorption. It is anticipated that the future will witness many more applications of PAN-based nanofibers in a wide variety of scientific discipline.

In the paper of **Wang-xi Zhang & Yan-zhi Wang *et al.* [7]** they discussed how the size of nanofibers change with applied voltage and characterization on oxidative stabilization. The concentration of PAN in solution is used and applied voltage changing with sample. As varying in applied voltage the diameter of nanofiber is changed means with increasing applied voltage the size of the diameter increasing because of electrostatic force is increased. If applied voltage is too high then it may possibly cause multiple jets which will reset in splitting and variance in fiber size. Oxidative stabilization process means heating PAN nanofibers at 200 to 300^0 C under air atmosphere and after that we go to carbonization process so that we got carbon nanofibers. Stabilization of PAN fibers result in ladder like structure this was done because the heat require to carbonize PAN fibers usually destroy the fiber before they become carbonized. PAN fibers need to stabilize first.

A Theron, E Zussmanand A L Yarin [8] developed a recyclable catalyst for generation of hydrogen from hydrosis of ammonia Borane. They have done fabrication of PAN supported by Pd-Pt alloy by simple electrospinning technique. This PAN/Pd-Pt composite nanofiber membrane possessed high catalytic activity and excellent recycling property for hydrogen generation.

In an article by **Sungho Lee, Jihoon Kim *et al.*[9]** PAN fibers were stabilized in convection oven with constant tension with 250^0C. The results of FTIP and gel fraction technique suggest that intra and inter molecular stabilization reactions occur simultaneously.

table 1 literature review

Sr. No.	Paper Title	Concen-tration	Voltage	Flow Rate mL/h	Distance	RPM	Diameter of nanofibers
1	A study on electrospinning of polyacrylonitrile nanofibers, Korean J. Chem. Eng., 28(1), 114-118 (2011)	13 %	11KV	0.293	20cm	900rpm	323.49-404nm
2	Adsorptive Removal of Malachite Green Dye by Functionalized Electrospun PAN Nanofibers, Membrane, Fibers and Polymers 2014, Vol.15, No.11, 2272-2282	12%	13KV	1 mL/h	12cm	900rpm	1736 Nm
3	Antimicrobial nano-fibrous membranes developed from electrospun polyacrylonitrile nanofibers, Journal of Membrane Science 369 (2011) 499–505	14%	25KV	1.3 mL/h	15cm	1000 rpm	1400nm
4	Carbon Nanofibers Prepared via Electrospinning, Adv. Mater. 2012, 24, 2547–2566	12%	20KV	0.34 mL/h	12cm	-	200nm
6	Carbon nanotube-reinforced Polyacrylonitrile nanofibers by vibration, electrospinning,PolymInt56:1367–1370 (2007)	18%	20KV	1.3 mL/h	8cm	-	1000nm
7	Characterization on oxidative stabilization of polyacrylonitrile nanofibers prepared by electrospinning, J Polym Res (2007) 14:467–474	8-12%	22KV	1 mL/h	10cm	-	500- 1000 Nm
9	Effect of polymer concentration on morphology of polyacrylonitrile(PAN) nanofibers prepared by electrospinning, NSNTAIJ, 7(4), 2013 [125-128]	9% 12% 16%	9KV	1 mL/h	10cm	-	100-250nm
10	Electrospinning and Microwave Absorption of	5% 7%	30-50 KV	0.9 mL/h	12cm	-	125-222nm

	Polyaniline/Polyacrylonitrile/ Multiwalled Carbon Nanotubes Nanocomposite Fibers, Fibers and Polymers 2014, Vol.15, No.11, 2290-2296	8%					
11	Electrospinning of Polyacrylonitrile Nanofibers and Simulation of Electric Field via Finite Element method, Nanomed Res J 2(2):87-92, Spring 2017	7% 9% 11%	15-20 KV	1.5 mL/h	10cm	-	100-202nm
12	Electrospinning of Polyacrylonitrile Nanofibers, Journal of Applied Polymer Science, Vol. 102, 1023–1029 (2006)	5- 20%	13-27 KV	1mL/h	10cm	1000 rpm	2000nm
13	Electrospun nanofiber membranes as ultrathin flexible super capacitors, The Royal Society of Chemistry 2017, 7, 12033–12040	10%	15KV	1 mL/h	12cm	-	500-900nm
14	Electrospun Polyacrylonitrile Nanofibers Containing a High Concentration of Well-Aligned Multiwall Carbon Nanotubes, Chem. Mater., Vol. 17, No. 5, 2005	7%	20-30KV	1.5 mL/h	12cm	-	200-500nm
15	Electrospun Polyacrylonitrile Nanofibers Supported Alloyed Pd-Pt Nanoparticles as Recyclable Catalysts for Hydrogen Generation from the Hydrolysis of Ammonia Borane, The Royal Society of Chemistry 2013, 00, 1-3	10%	15KV	1 mL/h	15cm	-	200-1500nm

Stabilization

Manufacturing carbon nanofibers from PAN Electrospuns are prepared by giving heat treatment cycles to nanofibers to improve their heat absorbance properties. Basically stabilization means we give low temperature to nanofibers by using furnace with having oxygen/nitrogen rich atmosphere. The temperature range of heat is from 180- 500^{0}C used, and time for heating is 1-5h [10].

PAN nanofibers are need to be under go for stabilization process because when fibers get carbonized in an inert atmosphere at high temperature they mostly destroyed, before they become carbon nanofibers [11]. Stabilization process has three techniques 1) Isothermal stabilization, 2) A stepwise increase in stabilization temperature, 3) One step stabilization. Nanofibers heated in furnace with oxygen environment and fibers adsorbed oxygen. PAN nanofibers have thermoplastic chain molecules after oxidation, these molecules converted into non-melteable ladder like polymer structure. By using stabilization process we increased the mechanical properties of the carbon nanofibers [12].

Sometime nanofibers were not properly stabilized, because of furnace or oven energy heat give from outer side of fiber to inner side of fiber so that heat was not distribute equally to nanofibers [13]. Sometime outer side of nanofiber becomes over stabilized but inner side remain under stabilized. This can make effect on quality of carbon nanofibers. This process is consumed more time so that it also consumes more energy which makes effect on cost of carbon nanofibers [14].

Carbonization process

The PAN nanofibers must be carbonized for making carbon nanofibers. In carbonization process, non-carbon element removes from PAN nanofibers. Carbonization is done in an inert environment of high heat. However the heat required carbonizing PAN fibers usually destroy the fibers before they become carbonized. Therefore, PAN fibers need to be stabilized [15].Not only the heating rate of stabilization but also the heating rate of carbonization has an influence on the final mechanical properties of the carbon fibres. For carbonization mostly Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) used. TGA and DSC use to get information about the heat treatment cycles during carbon fibre fabrication [16].

Applications of carbon Nanofibers

- Carbon nanofibers are widely used in medicinal industry. Due to high storage capacity it can be used for drug carriers and also used in wound healing process as they possess some antibacterial material [17].
- Carbon nanofibers are used as battery separators. These fibers provide a thin membrane for separating positive and negative electrodes to prevent electric short circuits but allow the ionic charge flow for current flowing [17].

- As a carbon nanofiber comes in form of sheets and folds they can be used for filtration purpose. Carbon nanofibers are used for air and liquid filtration. They provide high filtration with lower cost [17].
- Nanofibers have wide use in acoustic field. These fibers are work good as sound absorber. It decreases the production cost [18].
- Carbon nanofibers can be used as super capacitors for speedy charge and dischargeable batteries [18].
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Conclusions

Carbon nanofibers have wide application in various industries due to its high storage capacity, high porosity, high tensile strength and stability. Electrospinning method is a very efficient and easy method for preparing fibers. Stabilization for enhancing the heating capacity of the fibers by heating it in air in the presence of oxygen is one of the most efficient methods to conserve the fibres.

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