

A REVIEW OF ASSEMBLED POLYACRYLONITRILE-BASED CARBON NANOFIBER PREPARED ELECTROSPINNING PROCESS

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Electrospinning is a very simple and versatile process by which polymer nanofibers with diameters ranging from a few nanometers to several micrometers can be produced using an electrostatically driven jet of polymer solution (or polymer melt). Significant progress has been made in this process throughout the last decade and the resultant nanostructures have been exploited to a wide range of applications. An important feature of the electrospinning process is that electrospinning nanofibers are produced in atmospheric air and at room temperature. This paper reviews the assembled polyacrylonitrile (PAN)-based carbon nanofibers with various processing parameters such as electrical potential, distance between capillary and collector drum, solution flow rate (dope extrusion rate), and concentration of polymer solution. The average fiber diameter would increase with increasing concentration of the polymer solution and the flow rate. Therefore, the screen distance could also increase but the average electrical potential of the fibers diameter decreases. Electrospinning process can be conducted at higher electrical potentials, lower flow rate, nearer screen distance, and higher concentrations of dope.

Keywords: Electrospinning; nanofibers; polymer; flow rate; screen distance; electric potential.

1. Introduction

The market for carbon fibers is dominated by fibers made from polyacrylonitrile (PAN) due to their

combination of good mechanical properties (high strength, low-density composite materials, and high break strength (particularly tensile strength and

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reasonable cost).¹ The high strength and modulus of carbon fibers make them useful in the reinforcement of polymers, metals, carbons, and ceramics, despite the fibers' brittle nature. Carbon fibers prepared from PAN precursor fibers by conventional techniques have a minimum diameter between 5 μm and 7 μm . The bulk of production cost incurred during carbon fibers production is due to long heating times required to stabilize and carbonize the precursor fiber, in addition to engineering costs to maintain tension on fibers during stabilization.^{1–3}

Unlike conventional fiber spinning techniques, which are capable of producing fibers with diameters down to micron size range, electrostatic spinning, or electrospinning is capable of producing fibers with diameters in the nanometer size range, or “nanofibers”. In electrospinning, electrostatic forces are used in addition to mechanical forces to drive the fiber forming process. The resulting nanofibers are of substantial scientific and commercial interest, as they are thought to exhibit morphologies and properties different from conventional fibers.^{4–7} Normally, carbon fibers are prepared from PAN with conventional techniques (dry–wet spinning) and a spin dope range from 15–20 wt.% PAN copolymer solution using suitable solvents such as N,N-dimethylformamide. In air gap spinning, a spinneret is positioned several millimeters above a coagulation bath and jets/filaments are extruded vertically into the bath. The air gap spinning method permits the spin dope and the coagulation bath to be set at different temperatures and avoids the high stress caused by the spin dope coagulating on the surface of jets/filaments. Consequently, voids/flaws with sizes approximately tens of nanometers are commonly observed in the precursor fibers and the resulting carbon fibers. The existence of these defects is an

important reason for the mechanical strength of the currently produced carbon fibers only reaching a small percentage of the theoretically predicted value. Additionally, the large diameter of the precursor fibers is also responsible for the formation of structural, particularly sheath-core, structures during stabilization and carbonization.⁸

Electrospinning with PAN is capable of producing fibers in the nanometer diameter size range, or “nanofibers”. PAN permits faster rate of pyrolysis without much disturbance to its basic structure. The resulting nanofibers are of substantial scientific importance with extreme flexibility, low basis weight, cost effectiveness, and commercial interest, as morphologies and properties are different from conventional fibers.^{9,10}

Nanomaterials have become a research priority as biotechnology, defense and semiconductor industries in particular, are interested in potential applications of nanotechnology. Specifically, a substantial amount of research on nanoscale fibers is being conducted to meet the demands of their prospective application areas such as tissue engineering,^{11,12} membranes,¹³ nanoresonators,¹⁴ biomedical,¹⁵ and hydrophobic thin films.¹⁶

In general, the fabrication of carbon nanofibers involves six important steps. At the same time, there are several factors that need to be considered in order to ensure the success of each step. Among these steps, the pyrolysis process is the most important step and can be regarded as the heart of the carbon fibers production process. In general, the fabrication procedure of carbon nanofibers is shown in Fig. 1.¹⁷

Moreover, mechanical properties can be increased with electrospinning. Electrospinning can be conducted at the higher electric potential, lower flow rates, and higher concentration of dope.¹⁷ Mechanically

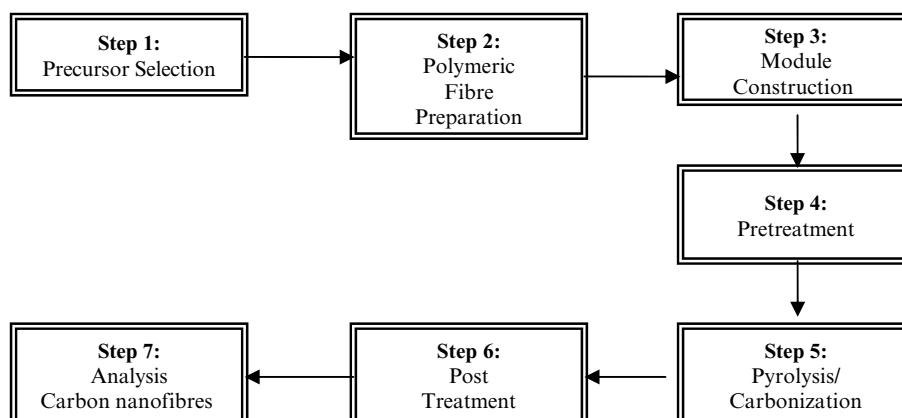


Fig. 1. Carbon nanofibers fabrication process.

useful PAN fibers can be produced by electrospinning, faster than conventional fibers, and therefore at a lower cost, and be a high-output means of producing submicron carbon fibers.⁸

In this study we concentrate on the current understanding of the electrospinning process and those parameters which influence the properties of the nanofibers produced from it. We also address issues of nanofibers structures and characteristics and discuss models proposed for processing instabilities due to the growing interest on nanofibers processed with specific bulk morphologies and surface topologies.

2. Precursor Selection

In the area of carbon fibers production, PAN fibers have been recognized as the most important and promising precursor for producing high-performance carbon fiber. It dominates nearly 90% of all worldwide sales of carbon fibers.¹⁸ There are numerous advantages of PAN fibers, including a high degree of molecular orientation, higher melting point (PAN fibers tend to decompose below melting the

point, T_m of $317^{\circ}\text{--}330^{\circ}\text{C}$), and a greater yield of the carbon fibers.¹⁹

PAN fibers form a thermally stable, highly oriented molecular structure when subjected to a low-temperature heat treatment, which is not significantly disrupted during the carbonization treatment at higher temperatures. This means that the resulting carbon fibers have good mechanical properties.¹⁹ One of the main problems of unsupported carbon membrane or hollow fiber is brittleness. Therefore, by applying PAN which is widely used in the production of high-strength carbon fibers, this problem can be minimized.²⁰

Schindler and Maier were the first researchers involved in the preparation of PAN carbon membrane based on their US patent published in 1990.²¹ They had prepared porous capillary carbon fiber by nitrogen gas pyrolysis system at pyrolysis temperatures ranging from 800°C to 1600°C . Before preoxidation and carbonization, the precursor fibers were subjected to pretreatment with hydrazine solution. Later in 1992, Yoneyama and Nishihara from Mitsubishi Rayon, Japan patented their invention on the preparation of porous hollow fiber carbon membranes.²²

Table 1. Advantages and disadvantages of various precursors to the carbon fiber production.^{19,23}

Precursors	Advantages	Disadvantages
Polyacrylonitrile (PAN)	<ol style="list-style-type: none"> 1. High degree of molecular orientation 2. Higher melting point 3. The yield of carbon fiber (50% of the original precursor mass) was almost double that of its yield from rayon 4. Form a thermally stable, highly oriented molecular structure when subjected to a low temperature heat treatment, which is not significantly disrupted during the carbonization treatment at higher temperature 5. High tensile strength could reach 100 GPa 6. High modulus could reach 1000 GPa 	<ol style="list-style-type: none"> 1. An expensive precursor
Pitch	<ol style="list-style-type: none"> 1. Mesophase precursor has been found to have mechanical properties similar to those obtained from PAN precursors 2. Better thermal and electrical conductivities than PAN-based carbon fiber 	<ol style="list-style-type: none"> 1. Intermediate strength and modulus properties 2. The overall yield from raw pitch is lower than PAN due to losses in the mesophase conversion step 3. Difficult to spin and the resultant fibers were more difficult to handle, therefore higher processing costs were required to make a spinnable pitch
Rayon	<ol style="list-style-type: none"> 1. Low density 2. Low heat conductivity and high strain 	<ol style="list-style-type: none"> 1. An expensive precursor
Vapor grown-based	<ol style="list-style-type: none"> 1. Structure close to graphite 	<ol style="list-style-type: none"> 1. Difficulty in processing condition

There are various types of precursors for the production of carbon fibers, namely, PAN, pitch (residual of petroleum product), coal, rayon, and latest development of vapor-grown fibers. Table 1 summarizes the advantages and disadvantages of carbon fibers, which should be useful for precursor selection. Based on Table 1, PAN has been found as the best precursor for producing high-performance carbon fiber as there are many advantages such as high degree of molecular orientation, thermal stability, higher melting point as well as low cost compared to other precursor materials. Because of this reason, it is no wonder why PAN-based fibers are widely used as a carbon fiber precursor and presently take up an overwhelming share which is more than 90% of the world's total carbon fiber production.¹⁹

Although PAN fibers are more expensive than rayon fibers, they are used extensively as a source of carbon fibers because their carbon yield is almost twice that of rayon.²³ Pitch carbon fibers have poor mechanical properties or poor reproducibility in their properties. Carbon nanofibers, such as other one-dimensional (1D) nanostructured materials, for example, nanowires, nanotubes, and molecular wires, are receiving increasing attention because of their large length to diameter ratio. They can be potentially used in nanocomposites,²⁴ hydrogen storage,²⁵ templates for nanotubes,²⁶ filters,²⁷ supercapacitors,^{28,29} bottom-up assembly of nanoelectronics, and photonics.³⁰

The nanometer's diameter size promises a high specific surface area and durable physical properties on the compression process.^{31,32} Reneker *et al.*²⁷ produced carbon nanofibers with diameters in the range from 100 nm to a few microns, from electrospinning PAN and mesophase pitch precursor fibers. Wang *et al.*, Kim *et al.*, and Zhou *et al.*^{33–35} produced carbon nanofibers from carbonizing electrospinning PAN nanofibers and studied their structures and conductivity. Hou *et al.*²⁶ reported a method to use the carbonized electrospinning PAN nanofibers as substrates for the formation of multi-walled carbon nanotubes.²⁶ Kim *et al.*²⁸ produced activated carbon nanofibers from PAN-based or pitch-based electrospinning fibers and studied the electrochemical properties of the carbon nanofibers web as an electrode for a supercapacitor.²⁸

3. Polymeric Fiber Preparation

Polymeric fibers or precursors for fabricating carbon fibers must be prepared at optimum conditions in

order to produce carbon fibers of high quality. In the case of poor quality polymeric fibers, a pyrolysis process cannot be expected to satisfactorily produce superior carbon membrane properties. Therefore, precursor fibers must be prepared in defect-free form in order to minimize problems in subsequent processing during the manufacture of carbon fibers.

PAN homopolymer is rarely used as a carbon fibers precursor since it initiates a retrograde core during the stabilization process due to partial melting caused by exothermic nature of oxidation process.³⁶ It is also generally not favorable for spinning purposes compared to its copolymers which are more soluble in solvents and easier to handle for preparation and storage.³⁷ The solubility of PAN and thermal properties of PAN fibers can be enhanced by the incorporation of either acidic, neutral, or hydrophilic moieties as comonomers during the polymerization or as spinning dope additives before the fabrication process. The addition of copolymer or additives is very essential in the PAN-based carbon fibers' dope formation. The incorporation of additives or comonomer can improve the processibility as well as the dyeability of the fibers.³⁸

The PAN homopolymer contains highly polar nitrile groups, hindering the alignment of macromolecular chains during spinning (particularly during stretching of as-spinning fibers). Additionally, the oxidative stabilization of PAN homopolymer occurs at a relatively high temperature, and the reaction is difficult to control due to a sudden and rapid evolution of heat. This surge of heat can cause the scission of macromolecular chain and make the resulting carbon fibers mechanically weak. Carbon nanofibers with the highest mechanical strength have been produced exclusively from the PAN copolymer precursors. The comonomer content usually ranges from 0.5 to 8 wt.%; typical comonomers include acids (such as itaconic acid), vinyl esters (such as methyl methacrylate), and others.³⁹ The inclusion of comonomer(s) partially disrupts the nitrile–nitrile interactions, rendering the copolymer more readily soluble in spinning solvent(s), allowing better macromolecular chain orientation in the precursor fibers, and making the stabilized and carbonized fibers more structurally homogeneous.⁴⁰

There are several solvents that are commercially used in preparing commercial dope solution. These include sodium thiocyanate, dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), N,N-dimethylcarbonylchloride

(DMCC), and N,N-dimethyltrichloroacetamide (DMTCAC).^{41–45} Among these solvents, DMAc and DMF showed good solubility in PAN polymer.

Numerous studies have shown that the electrospinning PAN fibers should possess the following characteristics: small diameter, maximum crystallinity, low comonomer contents, and high modulus for the preparation of good quality to prepare carbon nanofibers.^{46–52} Young's modulus of PAN precursor nanofibers is the best parameter representation of the carbon nanofibers' performance since there is a direct correlation between Young's modulus of primary precursor and the resulting carbon nanofibers.⁵³

4. Pretreatment of Precursor Fibers

Pretreatment is considered to be the most decisive step because it largely governs the final structure of the fiber and hence ultimate mechanical properties. Stabilization is carried out by controlled heating of the precursor fibers in an oxidizing atmosphere, e.g., air in the temperature range 180°C–300°C. The heating rate is usually 1°–2°C/min. Because of the chemical reactions involved, cyclization, dehydrogenation, aromatization, oxidation, and cross-linking occur and as a result of the conversion of C≡N bonds to C=N bonds a fully aromatic cyclized ladder-type structure forms (Fig. 2). This new structure is thermally stable (infusible). Also, it has been reported that during stabilization, CH₂ and CN groups disappear while C≡C, C=N, and =C–H

groups form. At the same time the color of precursor nanofibers changes gradually and finally turns black when carbonized. Research shows that optimum stabilization conditions lead to high-modulus carbon nanofibers. Too low temperatures lead to slow reactions and incomplete stabilization, where as too high temperatures can fuse or even burn the nanofibers.⁵⁵ It is also important that heating occurs with a very slow rate.

The main reactions taking place are cyclization, dehydrogenation, and oxidation. Dehydrogenation reactions precede cyclization, but they continue during and even after cyclization.⁵⁵ These reactions are responsible for the change in color of the precursor fibers to yellow, brown, and ultimate black. Berlin *et al.* believe it to be due to the development of polyene structure during heat treatment of PAN,⁵⁶ while others are of the opinion that the black color appears due to the formation of a condensed ring structure containing carbon–nitrogen double bond (Fig. 3).⁵⁸ This structure is often known as ladder structure. Most of the reactions are exothermic.

The cyclization reaction depends upon the initiation centers already present in the polymer. Another opinion is that it is initiated by the attack of oxygen.⁵⁸ The cyclization reaction is initiated by a radical mechanism in the homopolymer and by an ionic mechanism in the copolymers but the structure of the stabilized product does not differ very much.⁵⁹

Cyclization is not continuous throughout the chain. So, there are some uncyclized units left at

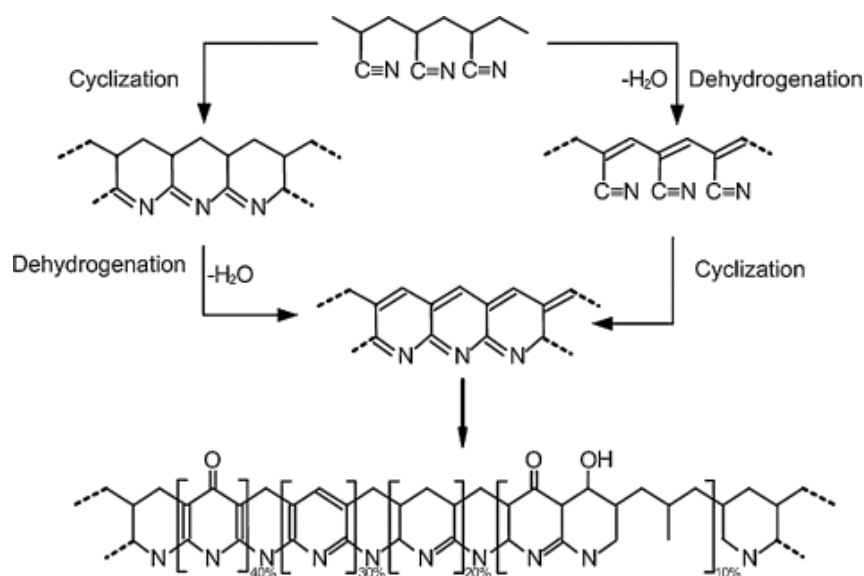


Fig. 2. Proposed chemistry of PAN stabilization.⁵⁴

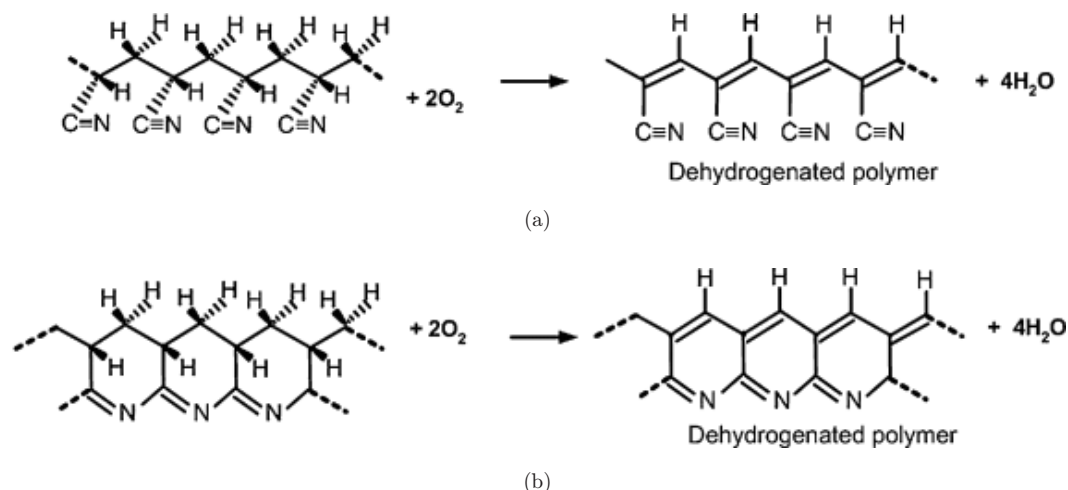


Fig. 3. The dehydrogenation reaction during stabilization process: (a) PAN polymer; (b) cyclized PAN.⁵⁷

random in the molecular chain.⁶⁰ These uncyclized units act as sites for chain scission and hence source of the evolved gases that account for the weight loss. The weight loss depends upon the average length of the cyclized sequence and the volatility of the fragments. Out of the various volatile compounds evolved, HCN is released during chain scission from the units which do not undergo cyclization and NH_3 is produced from the terminal imine structure.⁶¹ Preheating of PAN fibers in air causes dehydrogenation reaction, resulting in the formation of double bonds in the chain backbone, which impart greater stability to the chain. Thus, it is recommended that precursor fibers be heated slowly to get well-stabilized fibers. The stabilization process is greatly influenced by the variables of the tension on the fibers, the heat treatment temperature, the treatment medium, and get prestabilization treatment.

5. Pyrolysis/Carbonization Process

Pyrolysis (sometimes referred to as carbonization) is a process in which a suitable carbon precursor is heated in a controlled atmosphere (vacuum or inert) to the pyrolysis temperature at a specific heating rate for a sufficiently long thermal soak time. The pyrolysis process is conventionally used for the production of porous carbon fibers, and causes the product to have a certain microporosity of molecular dimensions that is responsible for the molecular sieve properties of carbon.⁶²

As in other fiber processing techniques, the final properties of the carbon nanofibers are largely determined by the precursor material and the

conditions used to form the precursor fiber. Post-treatment steps (e.g., stretching and carbonization) merely refine and perfect the as-spun structure. Hence, it was speculated that the fundamental structure and orientation of the fiber were established during the electrospinning process. Therefore, to obtain high-performance carbon nanofibers, it is important to understand the processing parameters involved in pyrolysis.^{63–67} Due to the special properties of the electrospinning PAN precursor and the typical dimensions of the carbonized nanofibers, high modulus and strength are each worthwhile goals to attempt to achieve. Carbonized microfibers are brittle, which suggests that they usually fail under mechanical load at critical flaws.⁶⁸ Due to the high L/d ratio of the nanofibers, reinforcement of composite materials would be expected to be expensive based on the Halpin–Tsai model.⁶⁹

In this process, all elements other than carbon are eliminated in the form of appropriate by-products,⁷⁰ and graphite-like structure is formed whereby stabilized precursor fibers are converted into carbon fibers. Carbonization is one of the necessary stages and it is as important as stabilization step in the conversion process from PAN fibers to high-strength carbon fibers.⁷¹ Carbonization is carried out in an inert atmosphere usually in Nitrogen condition without tension at heating temperatures between 300°C and 1000°C . In the stage of carbonization, fundamental changes of both chemical composition and physical properties can be seen.

During the carbonization stage, volatiles evolved and the carbon basal planes were formed. The formation of carbon basal planes was due to the cross-linking reaction and the elimination of

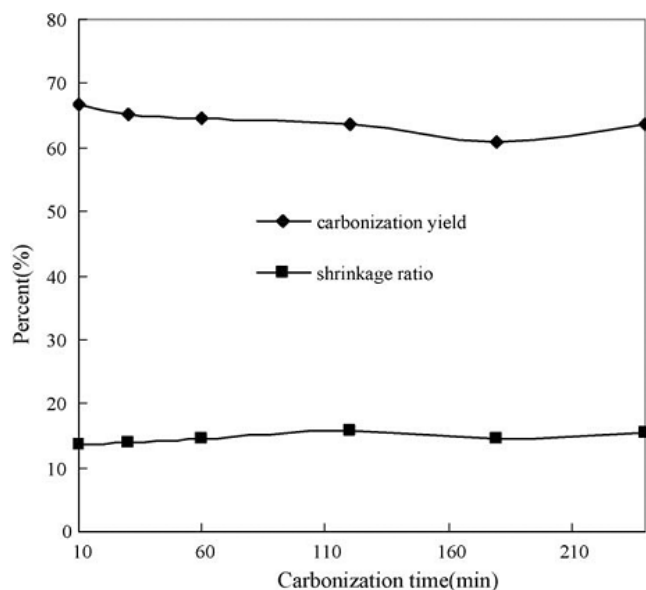


Fig. 4. Carbonization yield and shrinkage ratio of PAN-PHCFs versus carbonization time.⁶⁸

nitrogen. Figure 4 shows the variation of carbonization yield and shrinkage ratio of PAN-PHCFs with increasing carbonization time. The weight loss and the shrinkage ratio were determined from a change in weight and length before and after carbonization. The carbonization yield and the shrinkage ratio of PAN-PHCFs were calculated as follows:

$$\text{Carbonization yield (\%)} = \frac{\text{Weight after carbonization}}{\text{Weight before carbonization}} \times 100\%,$$

$$\text{Shrinkage ratio (\%)} = \frac{\text{Length before carbonization} - \text{length after carbonization}}{\text{Length before carbonization}} \times 100\%,$$

As shown in Fig. 4, the weight loss and shrinkage ratio of PAN-PHCFs are nearly unaffected with carbonization time, and the values of carbonization yield are about 64% and the values of shrinkage ratio are about 14%. It is suggested that the carbonization yield and shrinkage ratio of PAN-PHCF are not affected by carbonization time. During the carbonization stage, these volatiles are removed (i.e., H₂O, HCN, NH₃, CO, CO₂, N₂, and so on) to give carbon fibers with weight loss and shrinkage: the removal of volatiles from fibers becomes subdued with increasing carbonization time so that the weight loss and shrinkage ratio change little.⁶⁸

In this process, the heating rates in the two zones are crucial. The first zone, up to about 600°C, requires a low heating rate (less than 5°C/min) so as to make the mass transfer slow. A faster mass transfer at higher heating rates may cause surface irregularities in the form of pores due to the diffusion of involved gases.⁷² This zone is very crucial because it involves most of the chemical reactions and the evolution of volatile products. The evolution of water is due to the cross-linking of ladder polymer chains through the oxygen-containing groups. In the second zone, between 600°C and 1500°C, higher heating rates can be used because of the reduced possibility of damage due to exothermic reactions or the evolution of by-products since such reactions have already been completed by 600°C. This heating zone involves the evolution of N₂, HCN, and H₂. Nitrogen and hydrogen cyanide are evolved due to intermolecular cross-linking of the polymer chains, and hydrogen evolves as a result of dehydrogenation. During cross-linking, the carbon atoms of one cyclized sequence fit the spaces left by the nitrogen of the adjacent sequence.⁷³ This helps in the growth of a like structure in the lateral direction.

Oxidized PAN fibers are capable of producing high-performance carbon nanofibers in greater yield because they have preferentially an aromatic character, which prevents the backbone carbon chain from extensive splitting. In the case of PAN fibers stabilized in an inert atmosphere, the aromatization does not readily occur at low temperatures, and therefore it has to be induced at higher temperatures, which causes considerable splitting of the main carbon chain and results in a low yield and poor mechanical properties. The carbon fibers yield can further be enhanced by carbonizing oxidized PAN fibers in an atmosphere of HCl vapors⁷⁴ or by spinning the PAN fiber in a clean room.⁷⁵ Carbonization in HCl vapors decreases the amount of HCN by eliminating nitrogen in this fiber as ammonia. It also has a marked dehydrating action and eliminates oxygen as water vapor. Consequently, the yield of carbon increases. Electrospinning of the PAN nanofibers in a clean atmosphere results in a decrease in the average number of surface flaws, giving rise to carbon fiber with better mechanical properties. Tests conducted on the precursor fibers collected at different stages of heat treatment during the carbonization process showed that the modulus and the strength of the fibers increase rapidly up to about 1500°C. A decrease of the strength of the carbon nanofibers has been reported for heat-treatment

temperatures above 1500°C. However, the modulus keeps increasing at a slower rate.⁷⁶

In addition, electrospinning directly produces a web-structured fabric, which can be carbonized. When the carbonized web is used as an electrode, it does not require a second processing step to add a binder and an electric conductor such as carbon black. This is advantageous over then a nanotube method which needs the second step. The carbon nanofibers web thus obtained may be used for energy storage materials such as gas diffusion electrodes and supercapacitor electrodes. Yang *et al.*⁷⁷ and Kim *et al.*⁷⁸ obtained carbon nanofibers web from electrospinning in the absence of a catalyst and reported electrical properties of the web. The catalytic graphitization of electrospinning PAN-based nanofibers webs was carried out over the temperature range of 900–1500°C in nitrogen atmosphere. The electrical conductivity of the carbon nanofibers webs was increased with increasing carbonization temperature and content of the catalyst. These carbon nanofibers webs would be a good candidate for gas diffusion electrodes and supercapacitor electrodes because of high electrical conductivity.⁷⁹

6. Post-Treatment

The next step after carbonization will be graphitization. Carbonized fiber must undergo graphitization process for further improvement on the performance. Graphitization is the transformation of carbon structure into graphite structure by heat

treatment as well as thermal decomposition at high temperature processing.^{80–82} In this step, carbonized fibers are treated in argon condition at temperature up to 3000°C. At the end of the process, all carbonized fibers up to 99% are transformed into graphite structure because of thermal decomposition at high temperature processing.⁸⁰ A carbon fiber which was produced in this condition was in very high modulus fibers.

Following the carbonization process, the fibers have a structure with small crystallites. Perfecting the structure by increasing the size and alignment of the crystallites is achieved by heat-treating the fibers to temperatures beyond 1500°C. The process involves heating the carbon fibers under tension in an inert atmosphere, usually at about 2000–2500°C and sometimes up to 3000°C.⁸² Nitrogen cannot be used as the inert medium because above 2000°C it becomes active and forms cyanogen by reacting with the carbon fibers. Improvements in the crystal perfection are also achieved by passing an electric current through the carbon fibers when yarn is at 1800–3000°C.⁸³ Certain metal oxides such as chromium oxide, manganese dioxide, vanadium oxide, and molybdenum oxide, are used as catalysts for promoting the growth of crystallites during heat treatment of carbon fibers.⁸⁴

These fibers, high-temperature stabilized, can also be obtained by directly graphitizing to 2500°C at a rate of 100–200°C/min. These nanofibers still have the strength of about 2 GPa and modulus of 425 GPa, which is contrary to the general belief that the rate of carbonization should be slow and

Table 2. Mechanical properties of some commercially available PAN-based carbon fibers.¹⁹

Manufacturer	Product name	Tensile strength (MPa)	Yield modulus (GPa)	Strain to failure (%)
Hercules Inc. (USA)	AS-4	4000	235	1.6
	IM-6	4880	296	1.73
	IM-7	5300	276	1.5
Toray Industry (Japan)	T300	3530	230	1.5
	T800H	5490	294	1.9
	T1000G	6370	294	2.1
	T1000	7060	294	2.4
	M46J	4210	436	1.0
	M55J	3920	540	0.7
	M60J	3920	588	0.7
Amoco Corp. (USA)	Thornel T600	4160	241	1.72
	Thornel T700	3720	248	1.83
Toho Beslon (Japan)	HTA-7	3840	234	1.64
	ST111	4400	240	1.8
Mitsubishi Rayon (Japan)	Purofil TI	3330	245	1.40
	Purofil TI	2550	353	0.7

carbonization should be carried out in steps to produce the good-quality carbon nanofibers.⁸⁵ Some of the commercially available carbon fibers along with their mechanical properties are listed in Table 2.

7. Module Construction

This section describes the apparatus to be used for the electrospinning process, a complete picture of equipment design and experimental design of the process.²¹ The general outline of the equipment is as follows.

7.1. Design and procedure

The electrospinning apparatus consists basically of three components: a polymer reservoir, a high-voltage power supply, and a grounded collection device or target (Fig. 5). The polymer reservoir consists of a polymer either in solution or in the melt; a pendant drop of polymer solution is held at the end of a capillary tube through the use of a syringe pump (used to maintain constant back pressure).

An electrode, connected to a high-voltage power supply, is attached to the syringe tip and a voltage is applied. An electrical charge develops at the fluid's free surface and interacts with the external electric field resulting in the emission of a fluid jet that thins as it accelerates downfield. The surface of the pendant droplet distorts to form a conical protrusion and a straight jet is ejected from the surface of the drop as a consequence of electrical forces; the conical protrusion is often called a Taylor cone.⁸⁶ Farther downfield, the jet experiences a whipping instability that leads to bending and stretching of the jet; loops of increasing size are observed as the instability grows.⁸⁷

The following parameters and processing variables affect the electrospinning process: (i) system parameters such as molecular weight, molecular weight distribution and architecture (branched,

linear, etc.) of the polymer, and polymer solution properties (viscosity, conductivity, dielectric constant, and surface tension change carried by the spinning jet) and (ii) process parameters such as electric potential, flow rate, concentration, distance between the capillary and collector distance, ambient parameters (temperature, humidity, etc.), and finally motion of the target screen.⁸⁸

Several researchers have disclosed the details of the apparatus to achieve the research objectives of an electrospinning apparatus that was designed and constructed. The apparatus consists of two main devices, the sprayer and the collecting device.^{88–90}

7.1.1. Sprayer

The spraying setup (Fig. 6) has a glass spinneret with a needle of 0.3 mm inner diameter filled with polymer solution. The solution is filled to almost half of the glass spinneret, so that however viscous the solution is, it can be passed through the spinneret because of its own weight/pressure. The polymer solution is given a positive field with the help of a high-voltage power supply. The terminal wire (metal electrode) from the high-voltage power supply is held to the glass spinneret with the help of a rubber holder. The glass spinneret is held at a height from the ground with the help of a garolite stand and is at an inclined angle to the ground so as to facilitate fibers spraying on the drum surface (aluminum foil). The high-voltage power supply has a capacity ranging from 0 to 40 kV and the voltage can be increased at 1/10 of a kilovolt. Collecting drum is placed just below the spinneret to collect the waste polymer solution and stray charged fibers.

The groups working on electrospinning have adopted different solutions for the polymer solution feed. Some have simply opted for placing the capillary perpendicularly, letting the polymer fluid

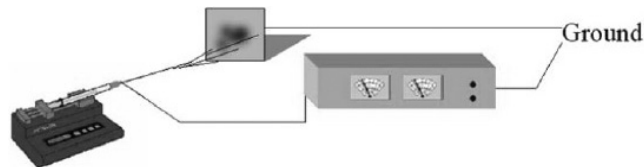


Fig. 5. Diagram of a typical solution electrospinning apparatus consisting of a syringe containing solution mounted on a syringe pump, a high voltage source, and a stationary, grounded target.⁸⁶

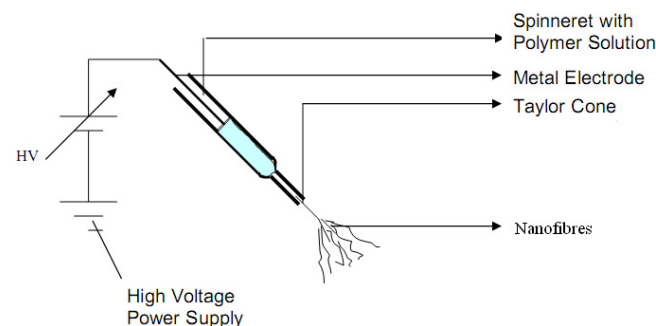


Fig. 6. Schematic of nanofibers spraying device.

drop with help of gravitation and laying the collector underneath.⁹¹ Sometimes the capillary can be tilted at a defined angle to control the flow.⁹² In other cases, the capillary was horizontal and a pump was used to initiate the droplet, the pump also being used in the case of vertical feeding.^{93,94} The electrode can be inserted either in the polymer fluid or placed on to the tip of the capillary if a syringe with a metal needle is issued.

7.1.2. Collecting device

The system of collection fibers (Fig. 5) includes a cylindrical drum with an external drive. The collector is a cylindrical drum (8" in diameter and 14" in length), made of polyvinyl chloride (PVC) pipe. The drum is held by a central shaft and is fixed to a wooden frame. A rotating drum for collection of fibers has been reported earlier. The PVC pipe and the wooden frame were used during the construction of the equipment to maintain the metal-free system. The wooden frame is built in such a way that there are slots in the frame. This facilitates the movement of the drum either upward or downward. This is done so that the vertical position of the cylinder can be adjusted to change the distance from the spinneret as per requirements. The drum is attached with a metal (brass) plate, a bush so as to complete the electrical connection (this has been explained in succeeding paragraphs with the help of suitable figures). The electrical connection is used as the negative terminal from the high-voltage equipment. Hence, the cylindrical drum serves as the negative terminal and thus aids in the collection of fibers.

One side of the pipe (right side on Fig. 7) is covered with a brass plate throughout its circumference. A metal rod is placed on a groove in the

drum throughout its length fixed at one end by the brass plate and the other end is free. The metal rod carries the electric field given by the brass plate. An aluminum foil is wound over the drum, covering the metal rod. This is done to maintain the same electric field over the entire drum surface. The negative end for the system is derived from the high-voltage power supply to the brass plate with the help of a connection wire and a bush, which is attached to the brass plate.

7.2. Direction of electrospinning

The parameters studied were polymer concentration, capillary-screen distance (C-SD), electric potential at the tip, and polymer solution flow rate. Different concentrations (15–25 wt.%) were electrospinning at different voltages (10–15 kV), capillary-screen distances (12–27 cm), and flow rates (3–7 mL/h).^{36,95} The electrospinning samples were collected on a stainless steel mesh (20 × 20) and later sputtered-coated with a 5 nm Pt layer. FESEM (Field Emission Scanning Electron Microscopy) was performed on these samples. Figure 8 shows the effect of C-SD on 15 wt.% that was electrospinning at 10 kV and 3 mL/h.

Distinct bead-like structures can be seen in the FESEM micrographs. It can also be seen that with increasing C-SD, the average fiber diameter decreases.⁹⁶ This is true for fibers spun at different concentrations, electrical potentials, and flow rates. Figure 9 shows the FESEM pictures of nanofibers that were electrospinning from 20 wt.% polymer solution at 10 kV and 3 mL/h.

Comparing Figs. 8 and 9, it can be inferred that the bead-like structure is predominant at lower concentrations. With increasing concentration of the polymer solution (keeping other parameters

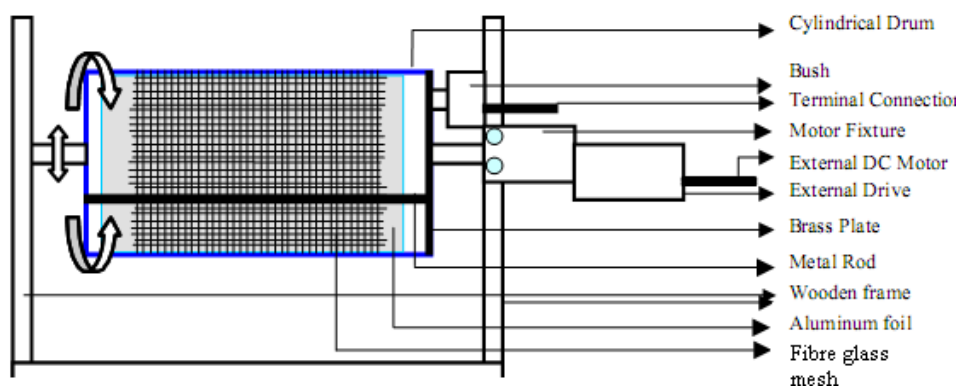


Fig. 7. Collecting device for electrospinning fibers.

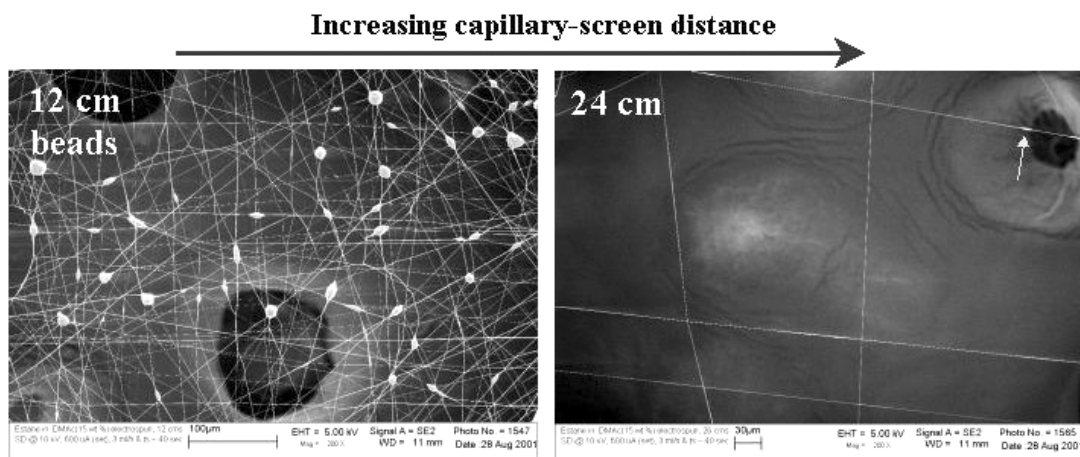


Fig. 8. Effect of increasing C-SD on 15 wt.% Estane electrospinning at 10 kV and 3 mL/h. Average diameter range 1 μm –148 nm and bead size 10 μm –2.5 nm. The average diameter of fibers and bead size decreases with increasing C-SD.⁹⁸

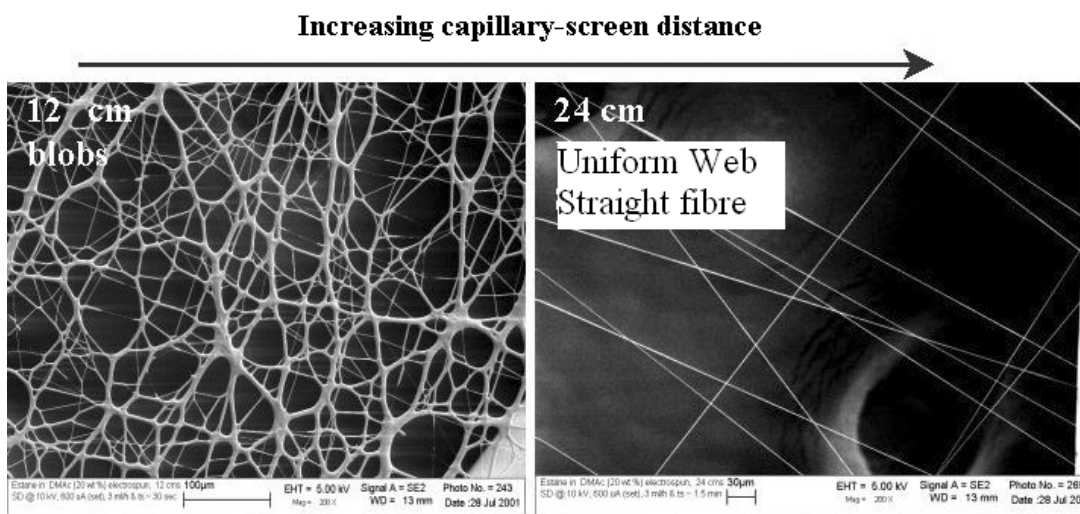


Fig. 9. Effect of increasing C-SD on 20 wt.% Estane electrospinning at 10 kV and 3 mL/h. Average diameter range 5 μm –333 nm. The average diameter of fibers decreases with increasing C-SD.⁹⁸

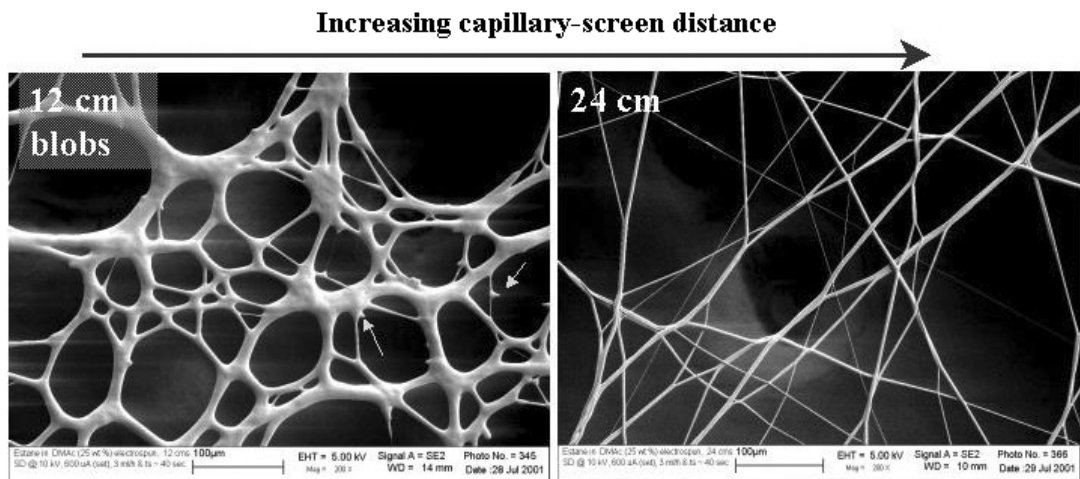


Fig. 10. Effect of increasing C-SD on 25 wt.% Estane electrospinning at 10 kV and 3 mL/h. Average diameter range 5 μm –905 nm. A broad distribution of fiber diameter was obtained.⁹⁸

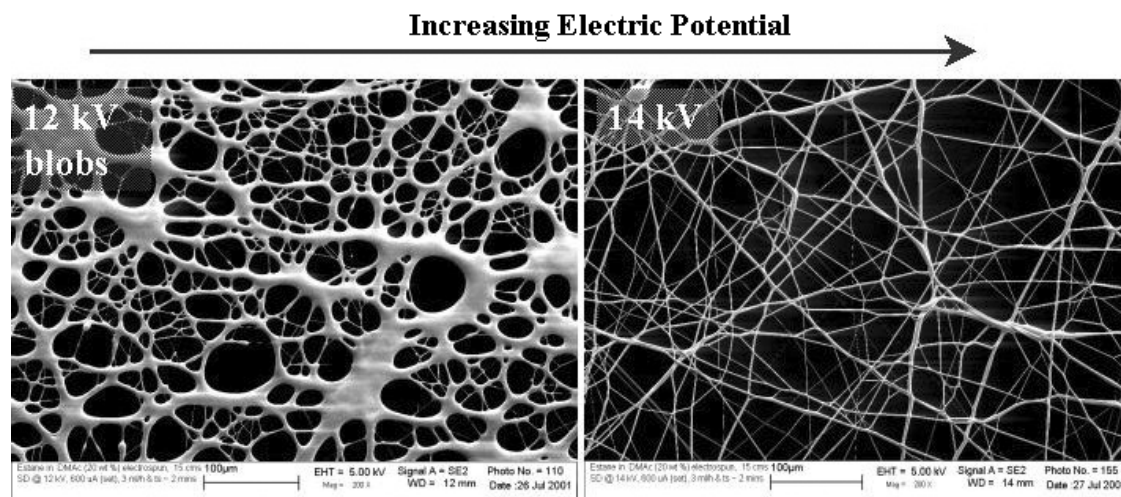


Fig. 11. Effect of electric potential on 20 wt.% Estane electrospinning at 3 mL/h and 15 cm C-SD. Diameters of fiber decrease with increasing voltage.⁹⁶

constant), the average fiber diameter increases.^{36,95–97} Again, with increasing C-SD the average fiber diameter decreases. Similar trends were observed at higher concentrations. At a lower C-SD (12 cm, 20 wt.%, Fig. 9) blobs are observed but they should not be mistaken to be beads. Figure 10 shows FESEM micrographs of nanofibers that are electrospinning at 10 kV and 3 mL/h.⁹⁸ Increasing electric potential (keeping other parameters constant) the fiber diameter decreases, as shown in Fig. 11.^{36,95,99}

With increasing electrical potential, the polymer jet is discharged with a greater electrostatic repulsion that causes it to undergo higher levels

of drawing stress. This results in the decrease of the fiber diameter. However, at higher electric potential (about 15 kV), the fiber diameter distribution becomes increasingly broader. Hence, the control of the process at high electric potential, flow rate and concentration becomes increasingly difficult. Figure 12 summarizes the effects of the different process parameters.

With increasing concentration of the polymer solution and flow rate (keeping other parameters constant), the average fiber diameter increases. Again, with increasing screen distance and electric potential the average fiber diameter decreases.

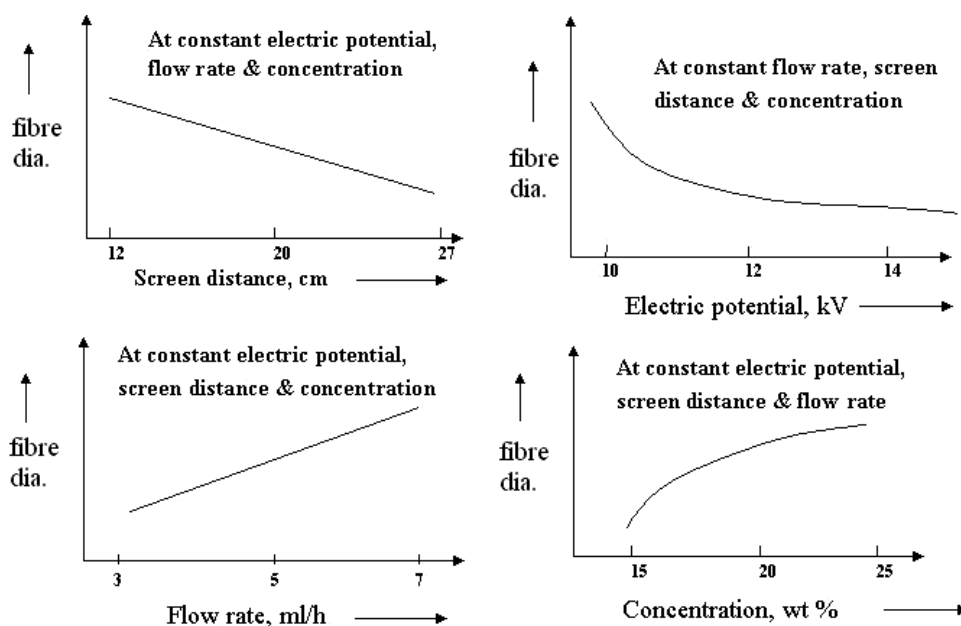


Fig. 12. Effect of process parameters on fiber diameter, produced by electrospinning.⁹⁶

The process parameters of electrospinning affect the result of nanofibers. To obtain a uniform fiber diameter web, it can be suggested that the electrospinning can be conducted at lower electrical potentials (around 10 kV), lower flow rates (around 3 mL/h), and polymer concentrations around 20 wt.%.

8. Conclusions

Of the four precursors, PAN is the most suitable to develop the carbon structure needed to produce high strength fibers and most carbon fibers manufactured commercially, today, are PAN-based. Carbon nanofibers prepared from PAN are more expensive than rayon but the carbon yield of PAN is approximately double that of rayon. High-performance carbon nanofibers are prepared with greater yield from oxidized PAN fibers due to their preferential aromatic character, which prevents the backbone carbon chain from extensive splitting during pyrolysis. Carbon nanofibers need to be handled with care because these are very brittle and fragile, which can be demanding.

Electrospinning is a very simple and versatile method of creating polymer-based high-functional and high-performance nanofibers that can revolutionize the world of structural materials. The process is versatile in that there is a wide range of polymer and biopolymer solutions or melts that can spin. Electrospinning with PAN is capable of producing fibers in the nanometer diameter size range or nanofibers. PAN permits faster rate of pyrolysis without much disturbance to its basic structure. The resulting nanofibers are of substantial scientific importance with extreme flexibility, low basis weight, cost effectiveness, and commercial interest, as morphologies and properties were different from conventional fibers.

An important characteristic of electrospinning is the ability to make fibers with diameters in the range of a few nanometers to a few microns. Consequently, these fibers have a large surface area per unit and smaller pore size in membrane, so that the membrane can be applied in medical applications, advanced aerodynamic, advanced composites to improve crack resistance and also air filtrations.

9. Future Work

The process of electrospinning is versatile in that there is a wide range of polymer and biopolymer solutions or melts that can be spinning to get high-performance nanofibers. In particular, integration of

nanofibers into useful devices requires nanofibers of well-controlled orientation, size, and other target characteristics as well as reproducibility in locating them in specific positions and orientations. With increasing concentration of the polymer solution and flow rate (keeping other parameters constant), the average fiber diameter increases. Again, with increasing screen distance and electrical potential (keeping other parameters constant), the average fibers diameter decreases. Electrospinning can be conducted at the higher electrical potentials, lower flow rates, and higher concentrations of dope to increase the mechanical properties of fibers.

The design and construction of process equipment for controllable and reproducible electrospinning could determine the character of instabilities revealed, satisfy potential implementation, and act as stimulus to provide new products. Moreover, to control over key performance parameters, the clarification of the fundamental electrodynamics of the electrospinning process and correlation to the polymer fluid characteristics must be reliably predicted and utilized. With these variables under control, the challenges of fully quantitative modeling of the electrospinning process should be feasible, including both stable and unstable operating regimes. Productivity improvement of the electrospinning process is also an essential feature and merits more studies.

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