NANOFIBER NONWOVENS: PRODUCTION TECHNOLOGIES, PROPERTIES, AND APPLICATIONS

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Abstract

Nanotechnology is a life-saving innovation that serves as a boon to mankind. It has offered novel products, which have superior control over a wide range of applications. An area of promise has been the development of nanofibers, which have diameters in the range of 1 nm to 100 nm. Nanofibers definitely hold great advantage over the microfibers in the domains of decontamination, filtration, and scaffolds for tissue engineering and wound dressings. It is projected that the nanofiber market worldwide will be worth more than $1 trillion. The discourse will deliberate upon the production technologies and their bottlenecks, properties, and applications of nanofiber nonwovens. State of the art, innovative and cost effective approach to produce nanofibers will also be discussed, through which one can produce nanofibers at production rates ~15,000 times that of conventional electrospinning

Introduction

Nanotechnology is a life-saving innovation that serves as a boon to mankind. It has offered novel products, which have superior control over a wide range of applications. An area of promise has been the development of nanofibers. According to the National Science Foundation (NSF), nanomaterials must have at least one dimension equal to or less than 100 nanometers. Hence, the diameter of nanofibers should be equal to or less than 100 nm. But in industrial jargon, submicron fibers, also termed as nanofibers, definitely hold great advantage over the microfibers in the domains of decontamination, catalysis, filtration, super absorbency, and as scaffolds for tissue engineering and wound dressings

Nanofibers have enormous specific surface area, high flexibility, and high thermal and electrical conductivity. Nanofibers have specific surface area from 10,000 to 1,000,000 square meters per kilogram. Three nanometer nanofibers may have about 40 percent molecules on the surface. Hence, the nanofibers have high surface energy and hence, have a remarkable capacity for reactivity of the catalysts, biocides, surface activity, tissue engineering, and filtration (Wang et al. 2005, Li et al. 2002, Ramakrishna et al. 2005)

Fuelled with the rapid growth of nanotechnology in the recent years, nanofiber technology too is burgeoning rapidly. Concerning the future of nanofiber, Ko opined that "$1 trillion are projected for electronic textile/wearable electronic markets; the $100 billion electronic packaging market; scaffolds for the $10 billion tissue engineering market projected by 2020; and the $5 billion automobile sensor and $1 billion biosensor market" (Ko 2009).

Nanofibers can be produced through various techniques like: islands-in-the-sea (Nakata et al. 2007), and drawing, nanofiber nonwovens can be produced by electrospinning, which is a popular technology due to simplicity and versatility of the process and a novel cutting edge modified melt blowing technique, being explored by researchers in our laboratory.

Electrospinning

Unlike, conventional fiber spinning methods like dry spinning or melt spinning, electrospinning uses electrostatic forces to stretch the polymer jet. In 1934, Anton Formhals patented an electrostatic technique to produce cellulose acetate microfibers. In 1969, Taylor derived a condition needed to transform the liquid droplet into a cone based on applied critical voltage, distance between the capillary, and the collector, the surface tension of the liquid, and the length and radius of the capillary (Taylor 1964). In 1971, Baumgarten was the first to electrospin submicron fibers.

In a typical electrospinning process, as shown in figure 1, a polymer melt/solution is fed through a capillary or a spinneret or a needle. Initially, as a result of surface tension, a pendant droplet of the melt/solution is formed at the tip of the spinneret or capillary. A high voltage, typically more than 5 kV, is applied to the solution, so that, the repulsive force overcomes the surface tension within the droplet. At a critical voltage, a Taylor cone is formed. On

further increasing the voltage, cone gets elongated into a jet (Teo et al. 2006). For a few centimeters, the jet is straight and stable near the tip of the spinneret. In the subsequent region, typically called as bending instability region, the planar waves cause the jet to move in a zigzag fashion along the capillary axis. The bending instability occurs as a result of either electrostatic stress relaxation of Coulombic forces, or the jet bends because of the nonuniformity of the charge density around the circumference due to lateral fluctuations or because of the torque due to dipolar component that is perpendicular to the jet axis or mutual repulsion of surface charges carried by the jet, (Reneker et al., 2000, Shin et al., 2001).

The entire jet moves off the axial path of the capillary and the jet breaks up in the subsequent oscillating-jet mode. Also, the plane in which the jet is elongating changes randomly. Due to the whipping action, the jet accelerates, stretches and hence, becomes significantly finer. The jet eventually breaks up into nanofibers as a result of repulsive electrostatic forces and the Coulombic fission associated with the increase in surface charge density at high amplitudes and weak bonding in the lateral direction. During the short flight of the jet from the spinneret up to the target, the solvent evaporates. Dry nanofibers collect in the form of a nonwoven web, on a grounded target. Copper plates, aluminum foil or plates and rotating drums have been used as targets.

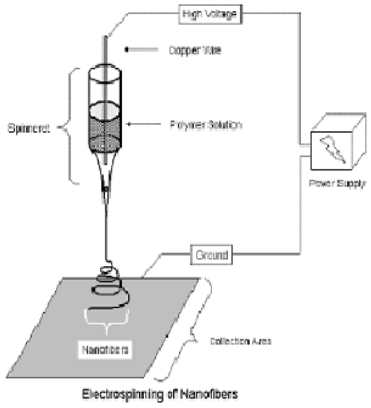

Figure 1: Schematic diagram for electro spinning, (Diller et al. 2003).

Electrospinning Parameters

In order to appreciate the process that enables the formation of various nanofibers during electrospinning, the affect of different parameters have to be understood. These parameters are summarized in Table 1. Solution properties influence electrospinability of a solution as well as the size of the nanofibers. At higher polymer concentration, the level of molecular entanglement increases, which is more conducive to fiber formation. The stability of the jet and more uniform fibers were produced at higher solution viscosity.

The conductivity of the liquid is a major factor in determining the onset of the jet formation. Highly conductive fluids drip whereas, there is no electrostatic charge built up in insulating materials. In the case of semi-conducting fluids (conductivity in the range of $10^{-6} - 10^{-8}\ \Omega^{-1}m^{-1}$), it was possible to form stable jets. When the voltage was increased, the cone height decreased, therefore increasing the angle of the cone from the axis. Due to the semi-conducting nature of the liquid, an electrical potential exists between the base of the cone and its apex. As a result, a tangential electric field is introduced in the direction of the flow, and electric shear stresses exist on the surface of the cone that can decrease its diameter as the jet length increases while maintaining a stable jet.

Table 1 Electrospinning Parameters

Polymer properties	**Solution properties**	**Process Parameters**
Molecular weight	Viscosity	Mass flow rate
Molecular-weight distribution	Concentration	Field strength
Solubility	Surface tension	Gap between the spinneret and the collector
Electrical conductivity	Vapor pressure	

The fiber diameter can be controlled by adjusting the flow rate, the conductivity of the spinning line, and the spinneret diameter (Ramakrishna et al. 2005, Theron et al. 2005). Fiber diameter decreases with the decrease in the spinneret capillary diameter and increase in the applied current. A direct relation between the nanofiber diameter and solution viscosity or solution concentration has been observed. It has been reported that increasing the voltage will decrease the diameter of the fibers produced. Increasing the voltage has the effect of pulling the polymer fluid away faster than the flow rate can replace it and therefore, the cone diminishes in size. Although, most of the electrospun fibers formed were cylindrical in shape however, others were capable of forming fibers that were flat, beaded, or ribbon-like.

Based on the current state of the art, it is obvious that nanofibers have a bright future and a large market potential, but only if the cost of these fibers can be dramatically reduced. Even niche products cannot afford to use fibers that cost more than $100 per pound. There has been several efforts to bring down the cost of electrospun nanofibers, but to date they have limited success in reducing the costs to commercially attractive levels. The mass rate of fiber production from a single jet is typically 0.1–1 gm/hr. Some of these issues are addressed in the reported two-layer electrospinning system. The multiple spinnerets or nozzles increased the production rate by 12 times than the single capillary arrangement. A high productivity capillaryless method by using a rotating cylinder has also been utilized to form fibers. The productivity was claimed to be between 15 - 18 gm/min. The mutual interference phenomenon amongst the multiple jets is a serious issue in multiple jet spinning. In terms of scaling up, and increasing the production rate of the electrospinning process, some challenges do exist, but can be overcome for example, using multiple jet electrospinning. Even though electrospinning can produce nanofibers, they are still prohibitively expensive and the most important challenge confronting electrospinning is the extremely low production rate. The mass rate of fiber production from a single jet is typically 0.1–1 gm/hr.

Although there is continuing effort to reduce the cost of production of nanofibers, commercial reality is still distant and unless the production rate of this technique can be increased by several orders of magnitude, the cost of nanofibers production will continue to relegate them to mostly a laboratory curiosity. Alternately, the innovative application of new technologies to produce nanofibers and nanofiber webs from thermoplastic polymers can be employed. In this study, a modified melt blowing process is being investigated, as a viable alternative.

Nanofiber Melt blowing

Melt blowing is a one-step process (Figure-2), in which high-velocity hot air blasts a molten thermoplastic polymer. A typical melt blowing process is a single integrated process, consisting of the following equipments: polymer-feeding systems, extruder, metering pumps, die assembly, web formation, and collector. Processing through extruder, metering pumps, filter, and up to die assembly is quite similar to melt spinning. However, die configuration and collection systems are designed specifically for melt blown process. A thermoplastic fiber-forming polymer is extruded through a linear die into converging streams of air that rapidly form fine fibers. The high velocity gas attenuates the fibers as they emerge from the spinneret. Moreover, the same air streams convey the fibers on to a collector. Enroute, these fibers are exposed to ambient air functioning as quench air. As the fibers settle on the collector, the bonding takes place at the fiber-to-fiber contact points and thereby a cohesive nonwoven

melt blown web is formed. Generally, vacuum is applied at the collector to facilitate disengagement of air from the fabric (Bhat et al. 2007).

Typical melt blown webs will have fibers in the range of 2-5 microns. Our recent research has shown that efforts to design and develop dies with smaller holes and larger number of holes are likely to allow the production of nanofibers. UTNRL has recently purchased a die from Hills Inc. Moreover, AG Russell, under license from Nonwoven Technologies, has donated a die to UTNRL for research and development of nanofibers.

Melt blowing process is popular, unique, and can be used to produce nanofibers at rates about 15,000 times higher than that possible from electrospinning. Hence, modified melt blown process would be a unique and novel process to produce nanofibers, at the industrial scale. The same polymers developed for synthetic staple fibers could be used. One of the advantages of melt-blown technology is to handle many different polymers as well as blends of polymers. So far, we have formed melt blown nanofibers from high MFR polypropylene, polyester and polybutylene terephthalate (PBT).

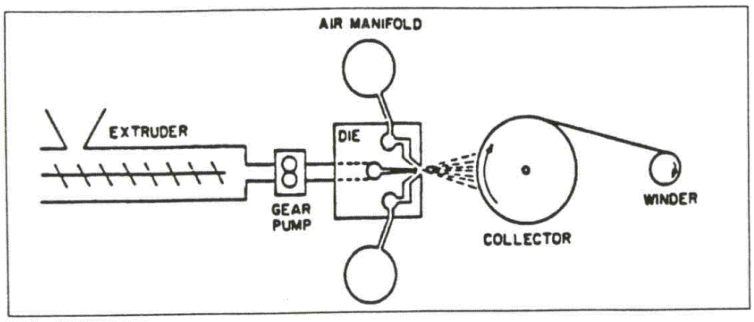

Figure 2: Schematic of a melt blowing line

Basically the same polymers developed for synthetic staple fibers could be used. So far, we have formed melt blown nanofibers from high MFR polypropylene, polyester and polybutylene terephthalate (PBT).

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As the melt emerges from the die holes, the high velocity hot air streams both from the top and bottom attenuate the polymer streams into finer filaments. As the hot air transports these filaments towards the collector screen, it draws in a large amount of ambient air (called as secondary air or quench air) that helps cool the filaments. Finally these fibers are laid onto the collecting screen surface, forming a self-bonded web (Bhat et al. 2007).

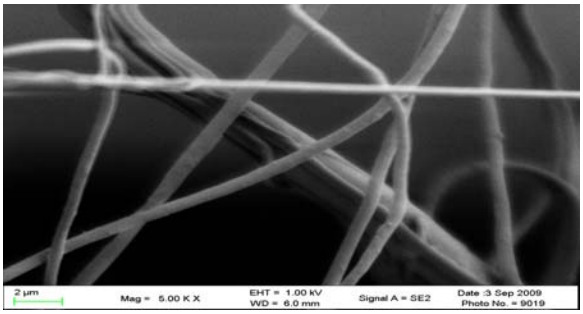

Figure 3: SEM image of a melt blown nanofiber web

As shown in Figure 3, the fibers in the web are highly entangled because of the turbulence in the air stream and random deposition, but there is a small bias in the machine direction due to some directionality imparted by the moving collector. The collector speed and the collector distance from the die nosepiece can be varied to produce a variety of melt-blown webs. Generally vacuum is applied to the inside of the collector screen to assist removal of hot air and enhance the fiber laying process.

The melt-blown web is usually wound onto a cylindrical cardboard core tubes and processed further according to the end-use requirement. The combination of fiber entanglement and fiber-to-fiber bonding generally produces enough web cohesion so that the web can be readily used without further bonding. However, additional bonding and finishing processes may further be applied to these melt-blown webs to alter the properties such as web strength, stiffness, and abrasion resistance. Thermal bonding is the most commonly used technique.

Nanofiber Melt blowing Parameters

In order to obtain desired properties of the melt blown web, there are many process variables related to machine as well as process inputs. Operating variables are online process variables that can be changed while machine is being operated. These variables include throughput and temperatures of polymer and air; die to collector distance (DCD), collector speed etc. Polymer throughput and airflow have influence on the final fiber diameter, fiber entanglement, basis weight and the attenuating zone. Polymer melt temperature, hot air temperature, and airflow rate affect the uniformity and the handle of the web, DCD affects the openness of the fabric, bonding among the fibers and basis weight.

Off-line variables include air gap, air angle, die setback, and die hole size. Die hole size along with die set back affects fiber size. Air gap affects the degree of fiber breakage by controlling the air exit pressure. Air angle controls airflow that decides the nature of the fibers in the web. As the air angle approaches 90°, turbulence increases, and causes random fiber distribution. At an angle of 30°, fibers are highly oriented.

Material variables include type of polymer, molecular weight and its distribution; melt viscosity, level of polymer additives, and polymer granule size. Generally, the melt blowing process is compatible with a variety and wide range of polymers in terms of viscosities and blends. As such, any thermoplastic polymer can be melt blown.

Process variables have a noticeable effect on the physical properties of resultant webs. The mean fiber diameter, tensile strength, initial modulus, stiffness and web density increase with increasing throughput. However, the decrease in both breaking strain and the energy required to break indicates the brittle nature of the web produced at higher throughput. Increasing fiber diameter was attributed to die swell and change in polymer-to-air ratio for a given airflow rate. Increase in airflow rate didn't result in any significant change in average fiber diameter. The die orifice size had only minimal effects on the average fiber diameter. The number of fibers and resulting surface area are greatly increased as fiber diameter decreases.

Web Characteristics

Melt blown nanofibers have diameter in the range of 150 to 1000 nm (Figure 4). The elongational force necessary to attenuate fiber diameter is provided by the aerodynamic drag. The fiber diameter attenuation is very rapid, as soon as it emerges from the die. However, it is observed that the fiber diameter attenuation continues to occur far from the die even though the drag force is not substantial. Finally, during lay down at the collector, again there is drag since the fibers come to a complete stop and as disengaging air continues to flow over. Melt blown nanofiber webs are soft, which can be attributed to the fineness of the nanofibers.

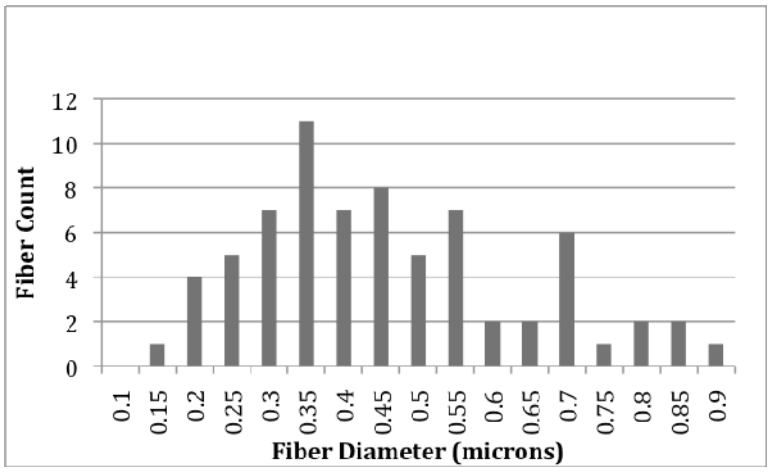

Figure 4: Fiber distribution of melt blown nanofibers

The web structure obtained by melt blowing process is generally isotropic, a typical characteristics of an air-laid process. Fiber orientation is generally random; however it is slightly biased in the collector belt moving direction. As a result, the physical properties are expected to be isotropic. Web strength is low as it is derived from mechanical entanglement and frictional forces among fibers. Nanofibers provide high surface area, which is useful for filtration applications. Fibers have a smooth surface texture and generally cross-section is circular.

The uniformity of the web is controlled by the distribution of fibers in the air stream, and the adjustment of vacuum at the collection system. Non-uniform distribution of the fiber in the air stream can be attributed to the non-uniformity of the secondary airflow from the surrounding. Generally, it is observed that the closer the die to the collector it yields more uniformity to the product.

Since melt blown web contains fine fibers of varied diameters, the cooling rates and the fiber temperatures are bound to vary. At the same time the fiber entanglement homogenizes individual fiber speeds and it is more-or-less independent of fiber diameter. Fine fibers cool faster. During melt blowing one can expect rapid stretching and nonisothermal cooling, which gives rise to a mesophase of low order.

Applications of Nanofiber Webs

Nanofibers nonwovens definitely hold great advantage over the microfibers in filtration because of lower drag force, lower pressure drop, higher permeability, higher interception and inertial impaction efficiency, higher particle capture efficiency, hence, much higher filtration efficiency, and longer filter life. Integrating nanofiber layer to current filter media improves the threshold of filterable particle size barrier. This market segment continues to be the largest single application. The applications include oil, fuel, and air filters, cartridge filters, clean room filters and facemask filter media.

MB materials in variety of physical forms are designed to pick up oily materials. The best-known application is the use of sorbents to pick up oil from the surface of water, such as encountered in an accidental oil spill, for mats in machine shops, and in industrial plants.

Incorporation of catalysts into the nanofibers enhances the reactivity of the catalysts, which can detoxify an agent. Nanofiber webs containing catalysts like POM, nano magnesium Oxide, modified β-Cyclodextrin, enzymes like OPAA, and biocides like N-Halamines, have greater oxidative/hydrolyzing activity against wide spectrum of chemical and biological warfare agents and can be an inner membrane of integrated self-decontaminating chemical and biological protective clothing.
The ability for natural polymers to match the demands of specialty markets creates a growing niche for them because the ability to tailor a product towards a particular consumer application is more important. Therefore, when the intrinsic properties of biopolymers are combined with the exciting nano-effects that nanofibrous mats have to offer, enhanced products can be manufactured.

Biopolymer nanofibrous mats have shown potential for applications within the medical field such as wound dressings, tissue engineering scaffolds for drug delivery (Travis et al. 2008). The success rate of artificially recreating the extracellular matrix and other tissue engineering applications depends on the properties of the scaffolds, such as their biocompatibility, degradability, and high specific surface area (Li et al. 2002). Nonwoven nanofibrous mats could conceivably resemble mechanical properties, degradation rate, as well as pore size, and the shape of the extracellular matrix (Schiffman et al. 2008). When the diameters of fibrous scaffolds are smaller than the diameter of a cell, cell proliferation is greater, (Liang et al. 2007).

Fuelled with the rapid growth of nanotechnology in the recent years, nanofiber technology too, is burgeoning rapidly.

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