

Polymeric Nano-Fibers and Modified Nano-Fibers Assembly in 3D Network for Different Potential Applications

M. Khayet*

Department of Applied Physics, Complutense University of Madrid, Spain

*Corresponding author: M. Khayet, Department of Applied Physics, Faculty of Physics, Complutense University of Madrid, Spain, Tel: +34-91-394-5185, E-mail: khayetm@fis.ucm.es

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Abstract

Polymeric nano-fiber based materials and their application is one of the research areas in materials science and nanotechnology. Nano-fibrous materials are receiving extensive research interest for applications in diverse fields as biosensors, optical and chemical sensors, stimuli-responsive or “smart” materials, bioreactors, drug delivery carriers, antibacterial materials, tissue engineering scaffolds, clean energy, electronic and semi-conductive materials, reinforced nano-composites, affinity membranes, etc. This is because of their important and interesting characteristics such as a very high surface area to volume ratio, tunable void volume fraction and inter-fiber space, flexibility in surface functionalities, good mechanical performance and malleability to construct a wide variety of nano-fiber based materials including beaded, ribbon, porous, and core-shell nano-fibers. Electro-spinning or electro-static spinning is the most considered technique for fabrication of nano-fibers. Synthetic and biopolymers, polymer blends, melts, nano-particle or drug-impregnated polymers, and ceramic precursors have been successfully used to produce electro-spun nano-fibers. Because the surface chemical and physical properties of the nano-fibers play an important role for a specific application, various surface modification techniques have been applied. A variety of bioactive molecules including anti-cancer drugs, enzymes and polysaccharides have been physically immobilized on the surface of nano-fibers.

Introduction

Fiber materials with diameters within the nanometer range when compared with micro-scale materials have several important characteristics such as a very high surface area to volume ratio, which for a nano-fiber can be as large as 103 times that of a microfiber, tunable void volume fraction or “porosity”, inter-fiber space or “pore size” ranging from ten nanometers to several micrometers, flexibility in surface functionalities, good mechanical performance and malleability to construct a wide variety of fiber sizes, shapes as well as the formation of different tailored membranes [1].

Polymer nano-fibers have been fabricated using physical, chemical, thermal and electrostatic techniques such as drawing [2], template synthesis [3], liquid-liquid phase separation [4], self-assembly [5], vapor-phase polymerization [6], and electro-spinning or electrostatic spinning [1]. This last technique is the most popular and preferred to use for preparation of polymeric nano-fibers because of its simplicity, versatility, economics (i.e. cost effective) and scale-up. Moreover, it is also employed to organize nano-fibers of various types (e.g. porous, hollow and core/sheath) into well-defined arrays or hierarchical architectures in three-dimensional network. Different fiber morphologies have been fabricated, such as beaded, ribbon, porous, and core-shell fibers [1]. A wide range of polymers

and copolymers can be used in this technique to produce fibers with different diameters from few micrometers down to tens of nanometers with controllable structures by adjusting electro-spinning process parameters [7].

The electro-spray process is known more than one century. Cooley [8] and Morton [9] patented an apparatus in which electric charges were used to electro-spray fluids. Between the first and second world wars, Formhals filed a series of US patents describing the experimental electro-spinning set-up for the production of polymer fibers using an electrostatic force [10-13]. Since then more than 50 patents on electro-spinning have been filed.

Electro-spinning

Electro-spinning is easily realized by applying a high voltage to a metallic needle connected to an electrically isolated tube through which the polymer liquid to be spun is circulated with a constant flow rate [1]. For example, when a positive voltage is applied to a metallic needle, the ions of the polymer solution of like-polarity will be forced to aggregate at the surface of the drop suspended at the tip of the needle. The electric field generated by the surface charge will cause the pendant drop of the polymer solution at the needle tip to deform into a conical

shape. The drop will experience two major types of electrostatic forces, the electrostatic repulsion between the surface charges and the Coulombic force exerted by the external electric field induced between the needle and the electrically grounded collector acting as a counter electrode (i.e. plate, rotating metal cylinder, or conducting coagulation bath). When a critical voltage is exceeded, the electrostatic forces act in opposition to, and overcome the polymer solution surface tension of the polymer liquid and a charged thin jet is erupted from the surface of the formed cone and moves towards the collector. As the electrified jet travels through the air space between the needle and the collector, it undergoes a stretching, elongation and whipping processes, while the solvent evaporates and a thin polymer fiber is then deposited on the form of a non-woven mat or over a support [1]. A random motion and instabilities of the electro-spinning jet are generally observed as a result of different interaction variables including electrostatic forces, gravity, air friction, polymer viscosity and surface tension. Interconnected aligned nano-fibers and assembled membranes with specific nanostructures can be prepared.

Electro-spinning materials

During last 10 years, electro-spinning has regained attention probably due to the emerging interest in materials science and nanotechnology as well as to the different possible advanced applications of electro-spun nano-fibers [14].

A number of electro-spun polymeric nano-fibers have been fabricated for applications in the diverse fields such as affinity membrane [15], biosensor, optical and chemical sensors [16], stimuli-responsive or “smart” materials [17], bioreactors [18], drug delivery carriers, antibacterial materials, tissue engineering scaffolds, wound dressing [19], clean energy [20], electronic and semi-conductive materials [21], air filtration [22], reinforced nano-composites [23], and membrane distillation [24]. More details on electro-spun nano-fibers and their applications may be found in [14].

Nano-fibers made of synthetic and natural polymers, polymer blends as well as melts, nano-particle- or drug-impregnated polymers, and ceramic precursors have been successfully produced by electro-spinning. Typically, a wide range of polymers like those used in conventional spinning have been used in electro-spinning including polyurethanes, polyamides, polyester, polystyrene, polyvinylidene fluoride, poly (ether imide), styrene-butadiene-styrene triblock copolymer, poly (vinylidene fluoride-co-hexafluoropropylene), etc. Biopolymers like proteins, DNA, collagen, polypeptides or others like electric conducting and photonic polymers and silk fibroin have also been used. For biomedical applications, poly (α-hydroxy acids), especially lactic acids, glycolic acids and their copolymers with 3-caprolactone, are the most commonly used among all biodegradable polymers [25,26].

Modification of electro-spun nano-fibers and nano-fibrous materials

Most of the polymer nano-fibers do not possess required specific functional groups and therefore must be functionalized for successful applications. Various surface modification techniques have been applied to render nano-fiber based materials suitable for a specific application. The methods used to modify the surface of polymer nano-fibers usually depend strongly on the nature of the fiber-forming polymer. Nano-fibers due to their size require less harsh reaction conditions and controlled reactions to prevent the morphology from being destroyed.

Surface modification is a powerful tool generally used to enhance the performance of electro-spun nano-fiber based materials and to increase the suitable functionality for specific applications. The methods used to modify the surface of polymer nano-fibers usually depend strongly on the nature of the fiber-forming polymer. Various surface modification techniques, categorized as physical or chemical processes, have been applied such as blending, coating, plasma treatment, wet mechanical method, surface graft polymerization, co-electro-spinning of surface active agents and polymers, molecule immobilization by physical absorption, assembly of nanoparticles on the surface of nano-fibers, layer-by-layer assembly, chemical immobilization, etc.

A variety of bioactive molecules including anti-cancer drugs, enzymes and polysaccharides as well as nano-particles have been entrapped within the interior of nano-fibers or physically immobilized on their surface. The surfaces of electro-spun nano-fibers were also chemically modified by immobilizing cell specific bioactive ligands to enhance cell adhesion and cell proliferation by mimicking the morphology and biological function of extracellular matrix. One must recognize that surface modification of polymers is a classic research topic, and it is still receiving extensive attention because new applications of polymeric materials have emerged, especially in the fields of biotechnology, bioengineering, and most recently in nanotechnology. In order to successfully apply adequately electro-spun nano-fiber in a given application, its surface should be chemically and/or physically modified during and/or after electro-spinning in order to provide the surface with the necessary properties for a successful application, such as chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity, antibacterial activity, etc. In some cases, physical surface modification methods can lead to changes in the chemical composition of the functional groups at the surface of the nano-fiber due to the removal or addition of a chemical group or activation of a chemical reaction on the surface of a material. For example, selective or ion-beam sputtering or selective cross-linking in the presence of plasma can induce chemical changes such as chain scissions, cross-linking, surface oxidation, depletion of small molecular weight fragments, and lead to the formation of a significant amount of hydroxyl groups, and even carbonyl groups.

Blending is the simplest and easiest method employed to functionalize a polymer nano-fiber. It is a physical approach consisting on the addition of blending ligand molecules into the polymer solution and then electro-spinning the polymer solution. No chemical bondings or attachments are involved between the polymer material and the modified species. It is a simple mixing of two or more materials that has been proven to be an effective method for polymer nano-fiber modification [27-29].

Plasma treatment of polymer materials has been commonly employed to tailor surface adhesion and wetting properties by changing the surface chemical composition [30,31]. Appropriate selection of a plasma source enabling the introduction of diverse functional groups on nano-fiber based materials is important [32].

Surface graft copolymerization is an easy and controllable introduction of graft chains to the surface of nano-fibrous materials without changing their bulk properties. This technique can be employed to modify the nano-fiber surface to obtain distinct properties through the choice of different monomers [33]. Surface graft copolymerization can be used to confer surface hydrophilicity and also to introduce multi-functional groups on nano-fiber surface for covalent immobilization of bioactive molecules. The surface graft copolymerization can be initiated via direct chemical modification, ozone, gamma rays, electron beams, plasma discharge or UV radiation treatment to generate free radicals for the polymerization [34].

The formation of ultra-thin surface layers following a bottom-up approach like self-assembly or applying surface coatings through synthetic chemistry on different types of surfaces is one of the research areas in materials science and nanotechnology. The main reason of such interest is the number of the applications requiring relatively defect-free surfaces with systematically engineered properties [35]. A surface modification method that allows surface coating with a thickness from a few nano- to several micro-meters through precise control has been realized by layer-by-layer polyelectrolyte multilayer assembly [36]. The method consists on an alternative layer-by-layer deposition of polyanions and polycations principally driven by an electrostatic force on charged substrates, resulting in self-assembled multilayer coating. The combination of layer-by-layer electrostatic assembly and electro-spinning provides the versatility to incorporate different functional polyelectrolytes to achieve multifunctional coatings.

Chemical methods are more effective surface modification techniques because of their flexibility for surface modification of thick nano-fibrous based materials [37]. These methods involve the introduction of one or more chemical species to a given surface in order to produce a surface with enhanced chemical and physical properties. Wet chemical oxidation treatments are commonly employed to introduce oxygen containing functional groups such as carbonyl, hydroxyl, and carboxyl groups at the surface of the nano-fibrous based materials [38]. The oxygen containing functional groups increase the polarity and the ability to hydrogen bond, which favors wet ability and adhesion.

Molecule immobilization on nano-fiber surface can be carried out using active surface agents following chemical functionalization, post-spinning modification, physical adsorption or by nano-particle polymer composites. Among these approaches, physical surface adsorption is the simplest one. Generally, electrostatic interaction, hydrogen bonding, hydrophobic interaction and van der Waals interaction can be used as a driving force for surface adsorption. Many functionalized composite nano-fibers were produced directly by electro-spinning polymer solutions containing nanoparticles of different types including metal alkoxide precursors. Incorporation of metal nano-particles in polymer matrices has allowed the development of materials with unique properties due to the nano-scale size and shape of the dispersed nanoparticles.

Covalent immobilization of active molecules on a polymer surface assures the long-term chemical stability of introduced chains in contrast to what occurs in physically coated polymer chains, and enhances cell adhesion and cell proliferation [33,39,40].

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