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1 Green electrospinning

Abstract: In the last two decades, electrospinning has grown in popularity; however, the majority of the setups are based on solution processing from toxic organic solvents. As green processing and environmental stewardship have also become important in recent years, for political and economic reasons, the subsequent increase in demand for the scaling up of electrospinning requires that an environmentally toxin-free process be championed. This book comprehensively addresses clean and safe electrospinning for the fabrication of green nanofibers and evaluates their potential applications.

Keywords: clean electrospinning, environmentally friendly electrospinning, green fibers, safe electrospinning, solvents

1.1 Introduction

Electrospinning is an efficient method that has been recognized for the fabrication of continuous polymer fibers with diameters down to a few nanometers. When the diameter of fibers decreases from micrometer to nanometer, several characteristics show up, such as a large surface area to volume ratio, flexibility, and mechanical performance. Initially, only polymers were accepted as fiber-forming materials. As time went on, ceramics and glasses were also considered as fiber precursors. By virtue of being a very simple and easily controlled technique, the utilization of electrospinning has spread into all fields of work, including biomedicine, pharmaceutics, filtration, energy, sensor, cosmetics, and food packaging.

In a typical electrospinning setup, there are three basic components necessary to the process: a high-voltage power supply, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen. During the process, the polymer solution or melt is pumped through the capillary tube and a high voltage is

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used to create an electrically charged jet of polymer out of the tube. The nozzle of the capillary tube serves as an electrode and a 100–500 kV m^{-1} electric field is applied. The solvent evaporates and the polymer solidifies while it is transported through the electric field. An interconnected web of fibers is therefore formed on the collecting screen. Considering that the solvent residuals are still present in the resulting nanofibrous mats, they may need to be post-modified to remove or neutralize the undesired solvent traces. The most common solvents for electrospinning are normally toxic organic solvents and, therefore, the presence of solvent residues will limit the use of obtained electrospun mats for any biomedical applications. It could also cause the operator to work under unhealthy conditions. Not only the toxicity of the electrospun scaffolds but also environmental concerns of the evaporating solvent have led to the concept of "Green Electrospinning" as a current issue (Figure 1.1).

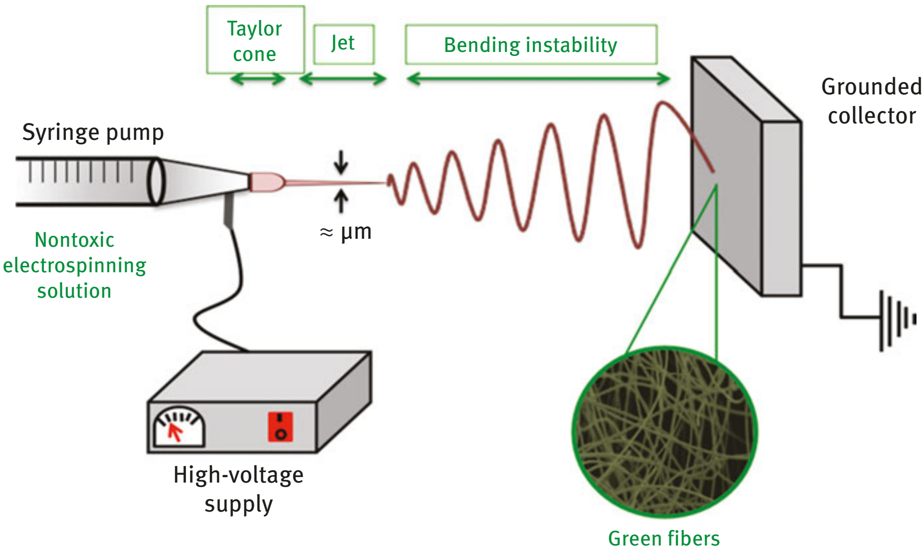


Figure 1.1: Schematic representation of green electrospinning setup.

Traditionally, electrospinning has relied heavily on the use of volatile organic solvents (VOCs) [1]. This is because solvents for electrospinning must not only be capable of dissolving the polymer chain but also be capable of evaporating within the short distance that separates the nozzle from the collector. Unfortunately, VOCs can be expensive, toxic, and hard to remove from the environment [2].

The number of journal articles using the term "green electrospinning" has been growing over the last 8 years. Green electrospinning is essentially the same or a similar procedure to traditional electrospinning and follows, therefore, the same overall physical principles that control the fiber diameter. Alterations in the procedure are attempted in order to remove the VOCs from the process and perhaps improve the recyclability and reusability of the various products and starting materials [1].

There are three main hazards in traditional electrospinning that arise due to the use of VOCs:

1) There are risks to the product user, particularly in the area of biomedicine, where materials will be implanted along with living tissue and cannot come in contact with toxic solvents.
2) Risks to the product producer: many VOCs are quickly brought into the ambient environment around electrospun fibers. If a chamber equipped with vacuum is a part of the electrospinning setup, the solvent exposure is minimized. However, trace amounts left in the porous fiber mats can overtime be dangerous to those working with the mats.
3) Risks to the environment: with the clear risk of VOCs and synthetic polymers accumulating within the air, waste that must be handled in particularly ways, with stray fibers that slowly accumulate in the soils (an unfortunate side effect of even washing of synthetic fiber clothes), and VOCs evaporating into the air effect our water, air, and soil quality [3–5].

Some particularly useful polymers for electrospinning, like polyimides, polyurethanes, and polyamides, require solvents such as dimethylformamide (DMF) or dimethylacetamide to be dissolved, which unfortunately are not volatile [6]. Other common harmful organic solvents may include strong acids such as formic acid, dichloromethane, ether, and chloroform. [7].

Green electrospinning would aim not only to reduce the use of VOCs and other toxic solvents, but to select suitable materials that produce more eco-friendly products. Some more common polymers due to their solubility in more aqueous solutions include polycaprolactone, poly(ethylene oxide) (PEO), and poly(vinyl alcohol), all of which are more easily degraded than polyolefins [1].

1.2 “Greener” electrospinning: on the way to a “truly green” electrospinning

As with many things in life, whether a glass is half empty or half full depends on the perspective of the observer. To consider a certain process “green” or not is one of these cases in which some people see the glass half full and others see the glass half empty. How “green” should an electrospinning process be to be called “green”?

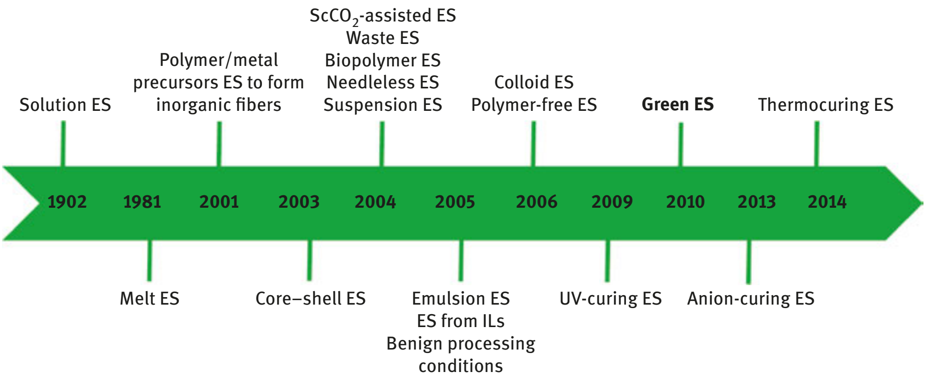
Any person reading this book is certainly aware of the popularity that the adjective "green" has attained in the last few years. The title of the book is the best demonstration. However, in these lines, we have no intention to open sterile controversies, but rather to act somehow as devil's advocate in our own field and incite in the reader a certain degree of self-criticism when confronted with the so-called – or "self-called" – green strategies. A rapid view of the literature will immediately show us that the concept of green fibers is not univocal and depends very much on the authors. For instance, when the resulting materials are used in biomedical applications, the biocompatibility of the final product is put in the foreground and then the label "green" seems to be almost self-explanatory. But were all chemicals and solvents used during the synthesis of the final biomaterial "truly green"? How green were the processing steps? It is obvious that such a "quantification" is far from trivial. Herein, we would like to point out a few concerns that should be kept in mind, regardless of whether the process is or not called "green":

a) The electrospinning of natural polymers, such as gelatin or chitosan, is commonly considered as "green," because the products can be considered as such. However, most of the solvents used in these processes are fluorinated (e.g., hexafluoro-2-propanol, tetrafluoroethylene, and trifluoroacetic acid). Similarly, there is a general trend to speak about "green electrospinning" when herbal extracts or essential oils are used in the process, no matter whether synthetic polymers or organic solvents are used.
b) In some of the processes classified as "green electrospinning," toxic reagents (e.g., cross-linkers or reducing agents) are used during the preparation of the fibers.
c) Some of the so-called green electrospinning processes involve high temperatures and high energy consumption. This situation applies to the preparation of most of the inorganic fibers, which are produced by electrospinning a template polymer and a metal precursor solution, followed by heat treatment steps. The energy consumption and the sustainability of the process are typically neglected when assigning the adjective "green."
d) Finally, there are cases in which water or so-called benign solvents (ethanol, limonene, acetic acid, etc.) are employed, but the final electrospun polymer is a conventional synthetic polymer. Can we then really speak about "green"?

The real fact is that most authors label electrospinning processes as "green" as soon as at least one of the "green" requisites is fulfilled, for instance, the use of water or a benign solvent, the presence of natural products or natural polymers, or biomedical applications and biocompatibility. A large majority of the examples presented in this book will fall within one of these cases. Processes being "truly green," in which none of the concerns stated above can be made, are rare and rather the exception. It is for this reason that, even if we are in the right track toward an environmentally friendly electrospinning, there is still plenty of room for optimization to achieve “greener” processes. This is the context in which this book should be placed and understood.

1.3 History of green electrospinning

It has been possible for many years to fabricate nanofibers via processes including drawing. However, none of these processes has allowed for the amount of control over the size of the fiber with as much consistency as found by using electrospinning. Electrospinning is a versatile technique that could be scaled up and could repeatedly yield reproducible results. While there have been patents filed for various electrospinning setups at the beginning of the twentieth century, it is only in the last two decades that industry and academia have been looking into using electrospinning to fabricate various nanofibrous mats for application in many fields. Scheme 1.1 presents an abbreviated version of the history of electrospinning with a more complete history having already been well documented in a number of literature including by Agarwal and Tucker [8, 9].

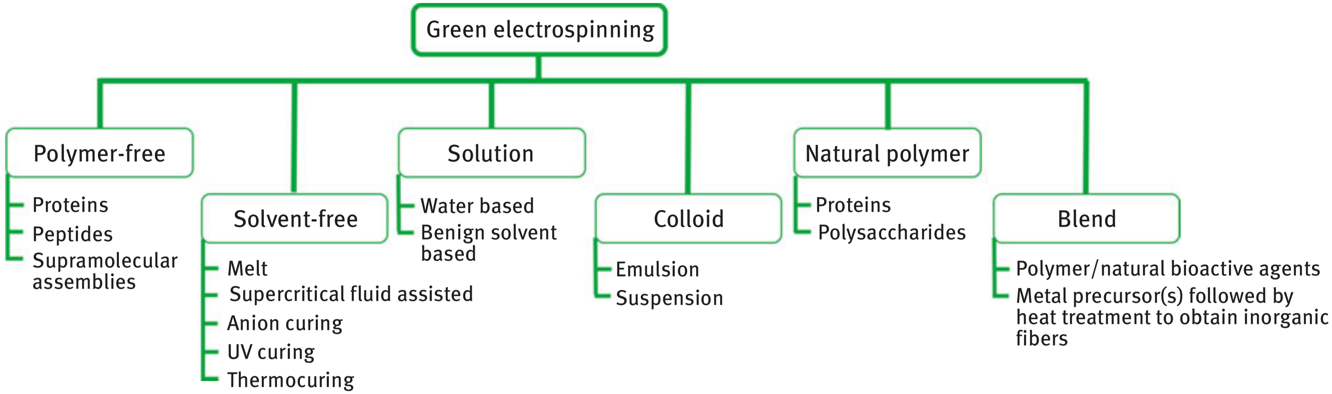


Scheme 1.1: Timeline of electrospinning.

From the eighteenth to the twentieth century, a great number of researchers had discovered the physical understanding of hydrodynamics and electrodynamics that makes up the basis for the electrospinning technique. Soon, a basic electrospinning apparatus was patented by Cooley and Morton between 1900 and 1902 [10, 11]. Approximately 30 years later, Anton Formhals patented several setups that produced yarns made out of electrospun fibers that were the progenitors of modern-day devices [12]. In 1936, C.L. Norton patented a device for the use of electrospinning from a melt rather than a solution and created the field of melt electrospinning [13]. A huge step was then made in the understanding of the electrospinning process: between 1964 and 1969, Sir Geoffrey Taylor contributed to the theoretical principles of electrospinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field, now known as the Taylor cone [14]. However, due to the slower fiber formation compared to conventional industrial fiber production techniques, the textiles industry did not fully take up electrospun fibers. During the latter quarter of the nineteenth century and the first two decades of the twenty-first century, a great number of advancements have been made in the theory and application of electrospinning. The parameters of solution electrospinning were defined for PEO solution in water [15] and PU in DMF [16].

In 2003, Huang et al. reported that almost 100 different polymers were transformed into ultrafine fibers using solution or melt electrospinning [17]. The processing of core–shell nano-/mesofibers by coelectrospinning of two components was described, providing the entrainment of a nonspinnable core material by a spinnable outer shell [18]. Li and Xia noticed that not only polymer solutions/melts but also liquid crystals, suspension of solid particles, and emulsions can be electrospun into nanofibers [19]. Yang and coworkers observed electrospinning of poly(*m*-phenylene isophthalamide) from its solution in ionic liquid for the first time [20]. In a different approach, by mixing colloidal silica particles with polymer solutions, followed by electrospinning, organic/inorganic fibers can be obtained and applied as photonic devices and microfluidic control devices [21]. In general, polymers have been taken as a structural framework for the fabrication of nanofibers through the entanglement and overlapping of the polymer chains. However, McKee successfully fabricated polymer-free nanofibers from phospholipids because of the cylindrical micelle formations in their concentrated solutions [22]. Compared to solution electrospinning, only a few groups have been interested in solvent-free electrospinning such as melt, supercritical CO_2-assisted, UV-curing, anion-curing, and thermocuring electrospinning, which eliminate the usage of toxic solvents and provide effective use of precursors [23]. Sun et al. [24] reported that the term “Green Electrospinning” was first used in 14th European Conference on Composite Materials (ECCM14) in 2010 by Ramakrishna and his coworkers. “Green/Safe/Clean Electrospinning,” which can be described as an approach to toxicology, safety, and environmental issues, can be accomplished by electrospinning from environmentally friendly solvents instead of toxic solvents, and from biodegradable natural polymers instead of synthetic polymers. Scheme 1.2 shows the classification of electrospinning with all processes that fall into the green category. Very commonly, green electrospinning has been related to emulsion and suspension electrospinning [1].

In this book, we extend the terminology to six groups: polymer-free, solvent-free, solution, and colloid electrospinning can be considered as *green processes*, while electrospinning from natural polymers and blends can be named as *green fibers*.



Scheme 1.2: Classification of Electrospinning referred to as 'Green'.

1.4 Structure of the book

After our succinct introduction to green electrospinning, we have discussed to what extent green electrospinning is truly green and touched upon the reality that some methods of green electrospinning yield better health and environmental outcomes than others. We have also given a brief the history of electrospinning and the advent and uses of green electrospinning. In Chapter 2, we will elaborate the green electrospinning in terms of green processes and green fibers.

We then discuss the different methods that are harnessed in green electrospinning. Chapters 3, 4, and 5 focus on polymer free, melt, and supercritical fluid–assisted electrospinning, respectively. In Chapters 6, 7, and 8, the focus is shifted to the use of water-based electrospinning and the use of natural and biopolymers (particularly cellulose and silk), respectively. In Chapter 9, we go over needless electrospinning. It is important to note that throughout the literature, some techniques for particular electrospun materials might take advantage of a number of the topics covered by various chapters, such as melt coaxial electrospinning [25]. Finally, Chapters 10, 11, and 12 deal with the applications of green electrospun fibers, including the formation of filters, biomedical materials, and batteries.

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