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I.Film: Using Electrospinning to Create Bioactive Films

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Abstract. With increasing competition between companies, they are increasingly striving to produce higher quality products and to improve their production processes, and the food industry is no different. In order to preserve food for longer, this type of company has dedicated its attention to intelligent packaging, capable of preserving food for longer and of acting as a sensor of the state of food. To develop a film capable of fulfilling the new ambitions of the companies various manufacturing processes have been studied. This document gives an overview of the electrospinning process, capable of producing nano-fibres of biological materials. This document aims to serve as a study base for the I.film project through the study of the process that will provide the polymer film with the necessary biological characteristics.

Introduction

With the constant growth of urban centers, people began to consume food products from larger commercial areas with more regularity. For the population this is their main means of acquiring food, reason why the quality and freshness of the food plays a fundamental role in the sales of the company and in the health of its consumers. In the packaged food sector, meat plays a key role, as it is one of the most sought-after products on the part of customers. Nowadays, our partner (Lusiaves) packaged poultry meat has a shelf life of approximately 9 days, and during these 9 days, the meat oxidizes and is becomes unfit for human consumption. It is important to take into account that the shelf life of the product starts when the animal is slaughtered, so it is understandable that some of the time is lost during processing and packaging, becoming fundamental the optimization of the process and the development of new materials. With the complexity of the distribution chains and the respective market enlargements, it is therefore essential to extend the validity of the food so that the producing companies can be competitive in the face of market demands.

The creation of intelligent and active functional films, capable of mitigating and / or retarding the oxidation of food, becomes a fundamental aspect to develop. It is therefore fundamental to develop a film capable of release controlled substances which retard the natural oxidation of the food and which also allows to act as a sensor for the oxidation of the food, by changing the color of the film. The use of this type of film allows a better quality control throughout the process, ensuring that it is possible to visually verify that the packaging environment was correct, also allowing less waste of food, as the objective is to almost double the shelf life time, from the standard 9 days to 15 days.

To create this material, it will be necessary that it be endowed with some different capacities, such as guarantee the impermeabilization of the packaging, guarantee the release of biological active agents capable of retarding the oxidation reactions of poultry meat, ensure regulatory compliance that regulates the area of food packaging and ensure that the film remains transparent, so that the customer can see the inside of the package.

In order to create a material with the desired characteristics, the group chose to work with a commercially available extruded film, the OPALEN HB 45 AF, and to use as bioactive element phycocolloid marine macroalgae. These algae have excellent antioxidant, antimicrobial, antifungal

and anti-cancer properties and their nano-fibers are compatible with most foods because they are water-soluble, have no odor or color.

To ensure that all features are met, it is then necessary to utilize a process capable of applying nanofibres of biological materials in previously extruded polymer films, because of the film processing temperatures, it would be impossible to incorporate these same materials into the extrusion process. In this way the electrospinning process emerged as a natural candidate for the processing of biological material as it allows the creation of nano-fibers within the desired temperature ranges.

Along this document the electrospinning process and its characteristics are going to be addressed to show how can this process solve the I.film project problem.

Electrospinning Technique

The electrospinning process was first patented in 1934 by Anton Formhals for the manufacture of textile yarns. It was only in the late 1990s that the electrospinning process became popular, after the Reneker's group carried out demonstrations of micro- and nano-scale polymer processing [1]. Since then, this technique has been preferred when compared to solvent casting or phase separation techniques, since it has a higher ratio between surface area and volume and a greater number of inter / intra-fibrous pores [2]. With the ability to manufacture nano-structures of various types of raw materials, from natural to synthetic polymers, scientists and industries have been increasingly developing applications for this nanostructure processing technique. Some of the new applications for the electrospinning technique include the creation of nano-fibers to act as biological and chemical nano-sensors and the creation of optical sensors through the use of flowering polymers [3,4]. In the present state of art will be approached some of the operating parameters of the manufacture of nano-fibers, such as parameters of electrospinning, parameters of the solution to be used and effects of the environment in the manufacture of fibers.

General vision on electrospinning process. The setup of an electrospinning equipment is typically composed of 4 components (Fig. 1):

1- A source of high voltage;
2- A capillary tube used as the first electrode (commonly a syringe needle);
3- A collector, used as second electrode;
4- A syringe to act as a pump;

There are variations of these components, such as dynamic collectors, coaxial capillary tubes and multiple capillary tubes [5].

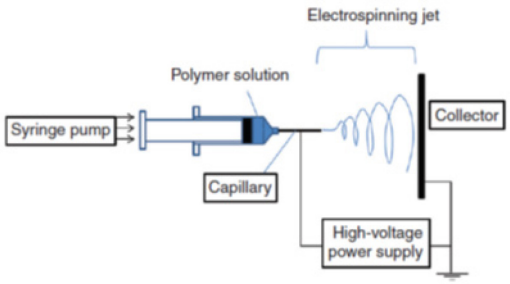

Fig. 1- Electrospinning basic setup (adapted from [6])

The electrospinning process begins when electrical charges are applied to the polymer solution through the syringe needle. This electric charge causes instability in the polymer solution by inducing charges in the polymer droplet present at the tip of the needle. At the same time, a reciprocal repulsion force produces forces that oppose surface tension, causing the polymer solution to flow toward the electric field. The increase of the electric field causes the spherical droplet to deform and assume a conical shape (Taylor's cone). At this stage, ultra fine nano-fibers emerge from the cone and are collected by a collector. During the process, the internal and external forces cause a whipping of the liquid towards the collector (Fig. 2), causing the polymer chains to be drawn, resulting in nano-fibers [2,6–8].

Fig. 2- Taylor cone (adapted from [2])

Electrospinning processing parameters. The operation of the electrospinning process depends on parameters related to the process itself, parameters related to the solution and parameters of the environment surrounding the process [9]. Among the parameters of the equipment we can highlight the electric field applied, the distance between the needle and the collector, flow rate and the diameter of the capillary tube.

Effect of applied voltage. The electric field is responsible for the creation of the Taylor cone and consequently the creation of ultrafine nano-fibers, through the application of a critical voltage to the polymer solution. The repulsion charges cause the polymer chain to be stretched, resulting in low-diameter nano-fibers. The use of stresses above the critical point results in coiled nano-fibers of higher diameter, since the Taylor cone will be smaller, resulting in a higher process velocity for the same flow rate (Fig. 3) [8,9]

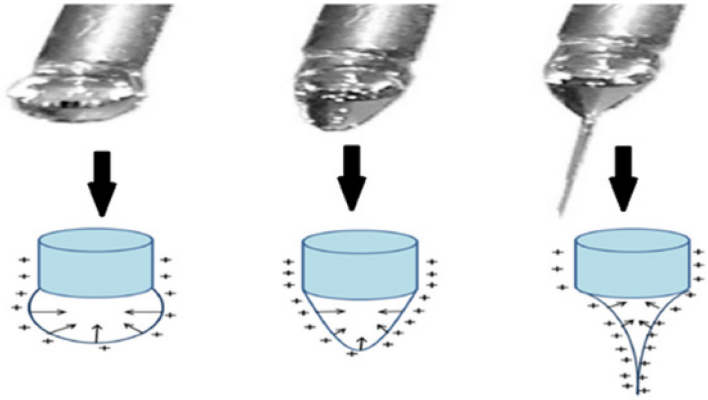

Fig. 3- Droplet variation with voltage (adapted from [2])

Effect of solution flow rate. The flow of polymer solution through the capillary tube determines the morphology of the nano-fibers produced, using a critical flow value, which varies depending on the polymer, to ensure the deposition of an aligned or misaligned form. Above the critical flow value, the diameter of the fibers increases, the deposition of the fibers becomes misaligned and consequently produces a material with higher porosity [10]. It is then preferred to maintain a minimum flow quotient to ensure equilibrium between the outlet of the polymer solution of the needle and its inlet [10–12].

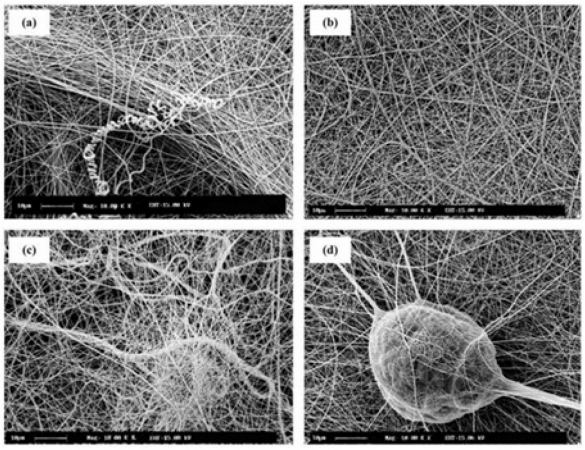

Fig. 4- SEM images with different flow rates (from the lowest to the biggest) (adapted from [12])

Effect of needle to collector distance and needle diameter. The distance between the metallic needle tip and collector plays an essential role in determining the morphology of an electrospun nanofiber. As ocours with the applied electric field, flow rate, and viscosity, the distance between the metallic needle tip and collector also varies with the polymer system. The deposition time, evaporation rate, whipping or instability interval easely affect the morphology of the nanofiber [13]. A vast number of research groups have studied the effect of the distance between the needle tip and collector and concluded that defective and large-diameter nano-fibers are formed when the distance is kept small and low-diameter nano-fibers are formed when this distance is bigger [13,14].

Effects of polymer concentration and solution viscosity. During electrospinning, the charged jet is subjected to uniaxial stretching and this phenomenon is significantly affected by the concentration of polymeric solution. As an example, when the concentration of the polymeric solution is low, the applied electric field and surface tension cause the entangled polymer chains to break into fragments before reaching the collector [15]. The morphologies of the beads depict and interesting shape change from a round droplet-like shape (with low viscosity solution) to a stretched droplet or ellipse to smooth fibers (with sufficient viscosity) as the solution viscosity changes, as shown in Fig. 5 [12]. It is then possible to conclude that the determination of the critical value of the concentration/viscosity is also essential to obtain beadles nano-fibers.

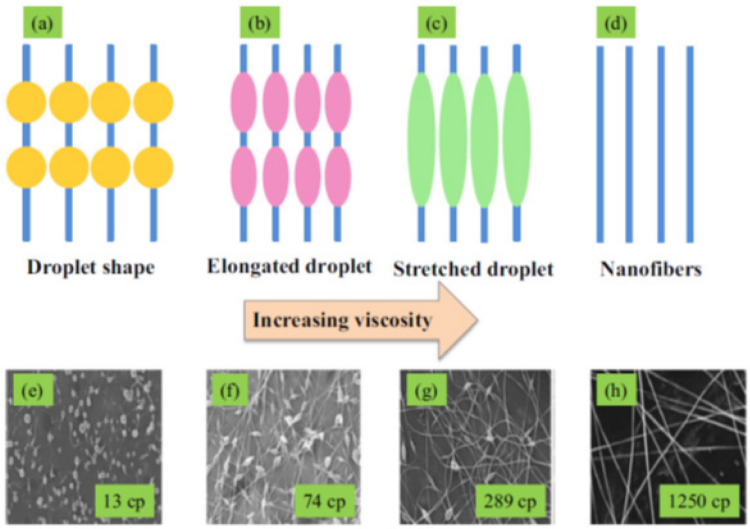

Fig. 5 - Variation in morphology of electrospun nano-fibers of PEO with viscosity: (a–d) schematic and (e–h) SEM micrographs. (adapted from [12,16,17])

Effects of solution conductivity. The solution conductivity not only affect the way the Taylor cone develops but also helps to control the nano-fibers diameter. Solutions with low conductivity will not have enough charge on the surface to create a Taylor cone, resulting in no electrospinning process. Increasing the conductivity of the solution to a critical value will not only increase the charge on the surface of the droplet to form Taylor cone but also it will cause decrease in the fiber diameter [18]. Electrospinning process depends on the Coulomb force between the charges on the surface of the fluid and the force duo to the external electric field. However, the formation of the Taylor cone is governed largely by the electrostatic force of the surface charges created by the applied external electric field. A conductive polymer solution will have sufficient free charges to move onto the surface of the fluid and form a Taylor cone and initiate the electrospinning process. The conductivity of the polymer solution could be controlled by the addition of an appropriate salt to the solution. Adding salt to the solution can affect the process of electrospinning in two ways: (1) increase of the surface charge density and increase of the electrostatic force generated by the applied field; (2) decrease in tangential electric field along the surface of the fluid. However, when this tangential electric field is extensively decreased, the electrostatic force along the surface of the fluid diminishes, which can affect negatively the formation of the Taylor cone. The stretching in the whipping region due to surface charges draws the fluid jet into the nanoscale [19].

Effect of the solvent in electrospinning. The selection of the solvent is one of the key factors for the formation of smooth and beadles electrospun nano-fibers. Usually two things must be kept in mind before selecting the solvent. First, the preferred solvents are the ones that are completely soluble. Second, the solvents should have a moderate boiling point, because the boiling point gives an indication of the volatility of the solvent. Generally volatile solvents are preferred as their high evaporation rates encourage the easy evaporation of the solvent from the nano-fibers, however, highly volatile solvents are mostly avoided because their low boiling points and high evaporation rates, causing the jet to dry at the needle tip [8].

The solvent also plays a vital role in the fabrication of highly porous nano-fibers. This can occur when a polymer is dissolved in two solvents, as one will act as a non-solvent. The different evaporation rates of the solvent and non-solvent will lead to phase separation and hence will result in the fabrication of highly porous electrospun nano-fibers [20].

Effect of humidity and temperature. Recently it has been reported that environmental factors, such humidity and temperature also affect the diameter and morphology of the nano-fibers. Humidity can cause changes in the nano-fibers diameter by controlling the solidification process of the charged jet, depending of the polymer chemical nature [21].

Electrospinning technique applied to i.FILM

In order to be able to incorporate this process into an automated extruded film production line, it will be necessary to make changes to existing equipment and / or redesign an equipment. The temperature limits are the set by the organic material, making its application through electrospinning to be framed at specific times of the creation of the extruded film. With this in mind, we defined as the best position for the electrospinning process, the place where the film is already being stretched and was rolled enough (dissipated enough temperature) to support the organic material (Fig. 6).

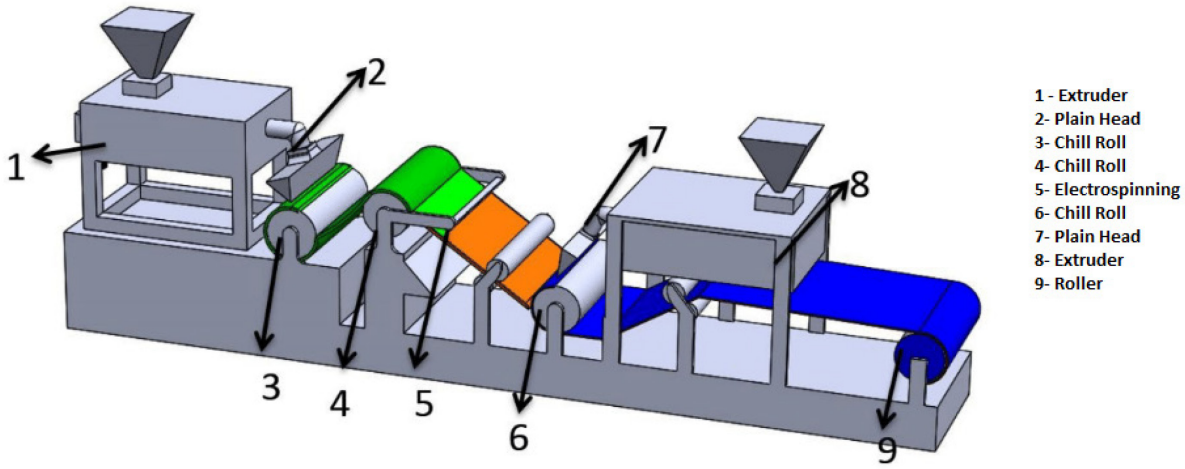

Fig. 6 - Machine Layout for I.film creation

On Stage 5, the basics of electrospinning are going to be applied using all the information described in this paper, and in Fig. 7 is possible to see the basic process applied on that particular stage.

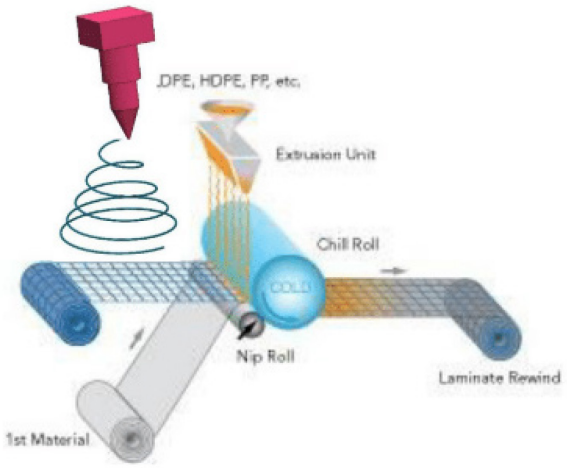

Fig. 7 - Applied electrospinning on thin films

After passing all the stages shown in Fig. 6, the material is ready to be applied on a continuous process of production in the factory plant. The objective is to have a final product as shown in Fig. 8, an apparently normal package, but with active proprieties, to preserve and warn the user regarding the state of the meat.

Fig. 8 - Example of the final package

Conclusions

According to the literature presented above, the electrospinning process allows the production of nano-fibers of biological materials, making it a viable process for the development of the necessary material for the project in question. The likely result will be the creation of a biomaterial layer of nanometric size, capable of releasing its biological agents that prevent the oxidation of poultry meat without compromising the quality of the food or the transparency of the film.

In order to perform a quality electrospinning process and ensure that the objectives are met, it is necessary to develop a solution of the biological material to be applied, so that the solution itself and the respective electrospinning parameters are fulfilled. After developing the solution, the parameters described above must be carefully addressed to ensure the final material success.

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