

Electrospun Structures for Dairy and Food Packaging Applications

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Abstract

Electrospinning is an electrostatic fiber fabrication technique, in which a nonwoven mat of long fibers can be assembled into a three-dimensional structure due to bending instability of the spinning jet. Owing to its versatile nature and potential for applications in diverse fields including food packaging has been gaining more interest. It is a flexible and easy tool for producing ultrathin sized by applying electrical force. In this process, altering the spinning solutions and process parameters could lead to fiber production with different properties enabling scope for different applications such as gas sensors, antimicrobial structures, water absorbing pads, etc.

Keywords: *Electrospun, food, fibres, packaging*

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INTRODUCTION

With a significant shift in India's demographic profile in favour of younger population, increasing surplus incomes, rising urbanization and changing lifestyles, food consumption patterns are steadily changing in favor of packaged and branded food products. Day-by-day consumers are becoming "smart" and expect their packaged food to be convenient, communicative and safe; in other words, it should be "smart". These trends and demands have resulted in emergence of various technologies such as active packaging including antimicrobial packaging, intelligent or smart packaging, biodegradable and nanocomposites packaging.

Recently, electrospinning technique has been extensively used for developing active and intelligent packaging systems for food applications, which include electrospun mats as absorbing and releasing agents and smart sensors. Electrospinning is an electrostatic fiber fabrication technique which has recently gained more interest and attention owing to its versatile nature and potential for applications in diverse fields such as medical devices in drug release, tissue scaffolds, wound dressings, and in chemical separation and purification application as affinity membranes, filter media, etc. It is a flexible and easy tool for producing ultrathin sized by applying

electrical force. Further they are utilized for commercial purposes, such as textiles finishing, cosmetics, household appliances and food contact materials [1]. In the electrospinning process, nonwoven mat of long fibers can be assembled into a three-dimensional structure due to bending instability of the spinning jet. Altering the spinning solutions and process parameters could lead to fiber production with different properties enabling scope for different application [2]. In the present article, the emerging applications of electrospinning in the area of dairy and food products packaging are briefly discussed.

PRINCIPLE OF ELECTROSPINNING AND ELECTROSPRAYING TECHNIQUE

Ultrathin fibres from conducting polymers can be produced by electrospinning. A conducting polymer solution or melted polymer is fed through nozzle jets to form droplets and subjected to a very high voltage (10–40 kV). Due to electrostatic force generated as a consequence of the applied high voltage, the fibres are drawn towards the collector where either the solvent evaporates or cooling occurs, resulting in the formation of nanofibres. An illustration of electrospinning apparatus setup is shown in Figure 1. In electrospinning, droplets are formed from the polymer solvent solution

emerging from the nozzle. The charged nozzle transfers its electrical energy to the droplet. When the liquid droplet gets charged due to high voltage applied to it, the electrostatic repulsion overcomes the surface tension leading to stretching of droplet. At a critical point the stream of liquid erupts from the surface, which is known as Taylor cone [3].

The principle of formation of Taylor cone and fiber is shown in Figure 2. At this point a liquefied polymer jet comes out from the tip of cone. When this jet enters the field formed between the nozzle and collecting wheel, it stretches and loops. The lengthening of the polymer fibre is due to simultaneous but separate events—the solvent evaporating from the polymer due to which it solidifies as a fibre and the charges within the polymer also repels each other, resulting in a noticeable reduction in the

diameter of the fibre with a significant increase in length, thus forming nanofibres. Electrospaying is a similar process to that of electrospinning. However when the viscosity of the liquid is sufficiently low, the liquid is drawn in the form of fine jet from the capillary nozzle due to electric charge and gets dispersed into droplets.

During electrospaying, the size of the droplets is mainly controlled by adjusting the voltage applied to the nozzle which affects the droplet charge and by changing the liquid flow rate [4]. Electrospinning and electrospaying both are intermingling process of polymer-based nanomaterials production. There is no difference in instrumental but the final product and applications are different and can be used separately or together.

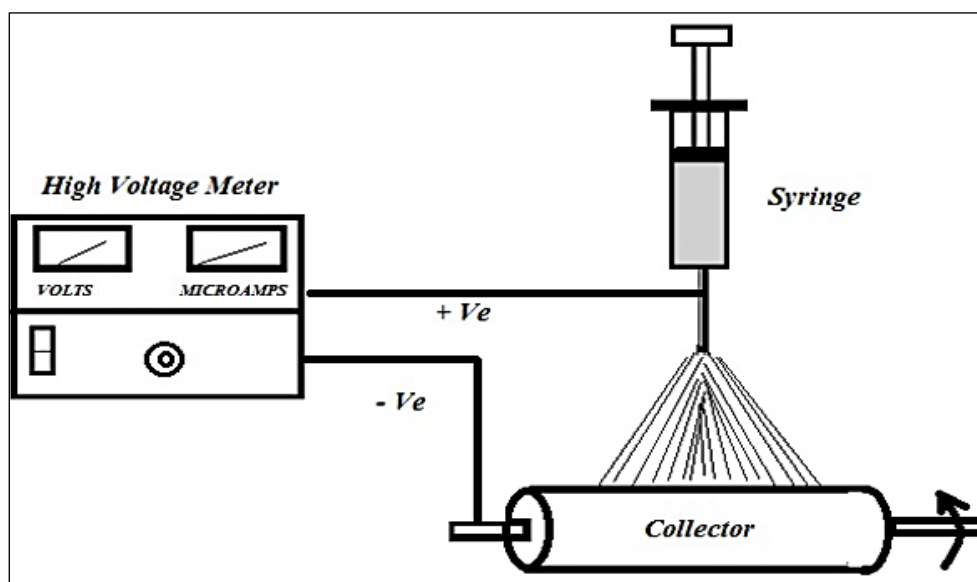


Fig. 1: Schematic Diagram of Electrospinning System [5].

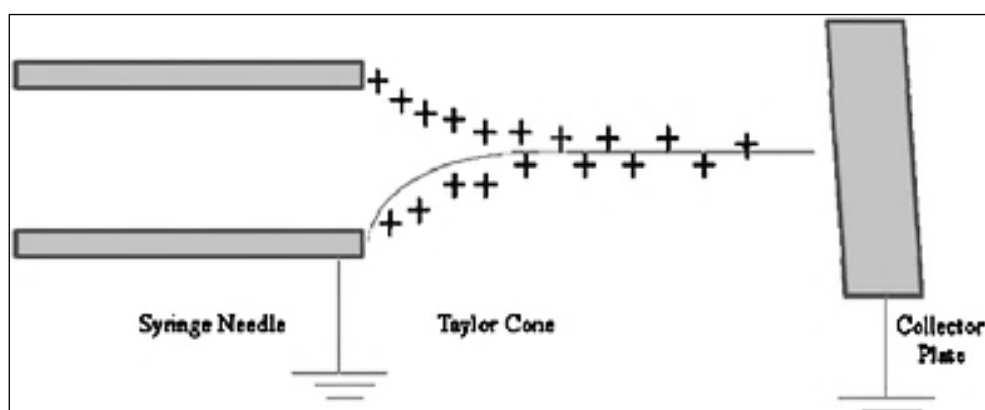


Fig. 2: Schematic Diagram of Taylor Cone Formation [6].

BASIC ELEMENTS OF ELECTROSPINNING APPARATUS

An electrospinning apparatus mainly consists of three essential components, namely (a) syringe pump, (b) high voltage setup, and (c) collector.

Syringe Pump

A metallic needle and syringe (spinneret) in which polymer solution (or melt) is filled can be attached to a syringe pump for obtaining a constant and controlled flow rate of the polymer solution [7].

High Voltage Setup

The driving force of the electrospinning process is a high-voltage DC power supply. The positive end of power supply is connected to metal needle (typically a syringe), which is already attached to the solution reservoir. Metallic collector is connected to negative electrode. The use of AC potentials is also feasible. This power supply may have multiple outputs, each of which may have a capacity in the range of 10–40 kV, to handle the electrospinning of single or multiple polymer reservoirs to obtain structures such as core and sheath [7].

Collector

The collector has a significant effect on the nanofibre productivity and structural arrangement of the fibres. Although several types of collectors (Figure 3) are available, a flat, conductive metal plate typically made of aluminum or any other conducting material is most popular one. A collector usually acts as a conductive substrate for collecting the charged fibers during the electrospinning process. The flying fibres get attracted by the conducting metal plate surface and settle on it. Gradual deposition of the nanofibres will create nanofibre web matrix or electrospun mat. Aluminum foil is used as a collector but there are many kind of collectors used for different applications such as wire mesh, rotating rods or wheel, pin, grids, parallel or gridded bar, liquid bath and so on [8].

TYPES OF COLLECTORS

Static Plain Surface Collector

Static collector comprises of an electrically continual and flat electrode. Aluminum or any conducting flat surface can be used. It is a very simple and easy to fabricate type of collector. This type of collector can be used in initial stages in the development of a nanofibre mat.

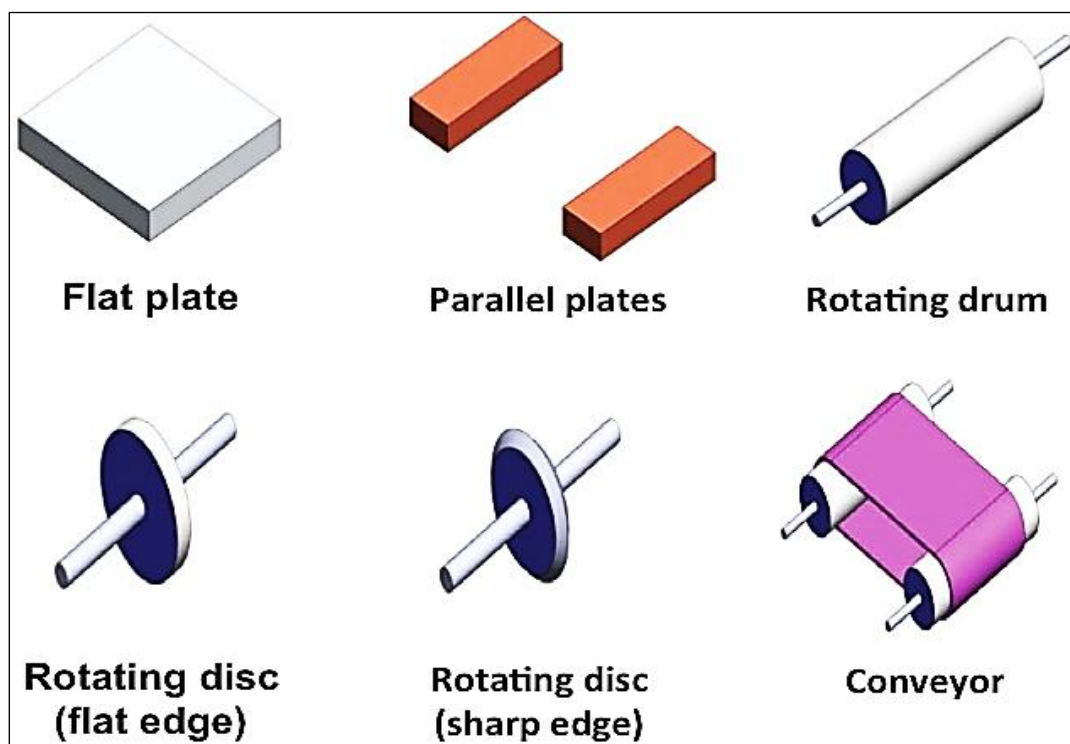


Fig. 3: Different Types of Collector Arrangement [9].

The main features of this collector include (a) production of random order of individual fibres, (b) simple construction without moving parts, and (c) homogenous layers.

Static Wire Collector

Thin conductive wires are fixed at certain distance from each other forms the static wire collector. During electrospinning the fibres gets oriented in a particular direction either perpendicular to the conductive wires or between the conductive wires. Geometry and physical parameters of the collector determines the degree of alignment. It is a simplest way to achieve the very good internal structuring of nanofibre materials because of which it is frequently used for the development of new materials as the base collector to prepare smaller samples with an aligned structure. The main features of this collector are (a) high degree of fiber alignment, (b) simple construction, and (c) variable air gap can be maintained.

Rotating Drum Collector

The shape of rotating collector is like a drum whose surface is smooth and electrically continual. Drum speed can be adjusted as per the requirement of fibre alignment. At slow speed, the fibers are randomly deposited on the drum surface but at high speeds, fibres get deposited in the preferred direction. The main features include (a) high degree of fiber alignment at high revolutions, (b) one parameter optimization, and (c) homogenous layers.

Rotating Wire Collector

The rotating wire collector is composed of thin wires arranged vertically and at equal distance from the axis of rotation. At very low speeds, the fibres are deposited between the conductive wires with the principle for the creation of aligned fibres being same as in the case of the rotating drum collector. The degree of alignment of the individual fibres gets increased due to the combination of electrostatic and mechanical forces. A very good fibre alignment can be obtained at much lower collector speeds as compared to those of rotating drum collector. The main features of rotating wire collector are (a) a very high degree of fiber alignment at high revolutions, (b) provision of optimization of linear surface

velocity and void gap size, and (c) variable wire void gap size.

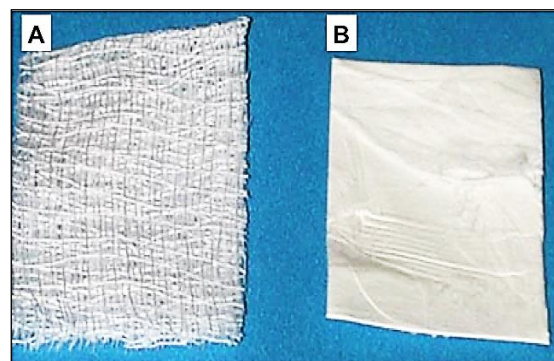


Fig. 4: A Glance of (A) Cotton Gauze and; (B) An Electrospun Bovine Fibrinogen Mat.

CURRENT APPLICATIONS OF ELECTROSPUN STRUCTURES

Improvement of Properties of Packaging Material

A new way to develop high gas and vapor barrier packaging material is to combine various nanolayers by using an electrospinning process [10]. Use of electrospinning for the manufacture of reinforced fibres offers the advantage of producing a subset of very fine diameter fibres within the fibrous mat (Figure 4). This subset of fine fibres would be able to interact efficiently with the matrix in which they are dispersed. Polyhydroxyalkanoates (PHA) packaging film with high oxygen barrier is obtained by means of nanostructured electrospun interlayers of zein and zein interlayer thickness increased with the electrospinning deposition time [11].

Oxygen permeability values were measured to drop by a maximum of 70% in both PHA and polylactic acid multilayer systems by the addition of electrospun zein nanofibres. The multilayer structure gets compressed due to the introduction of regularly drawn electrospun zein fibres, which are forced to align in thick bundles of ultrathin fibres along the interlayer direction and thus decreasing the oxygen permeability. Apart from pure zein nanofibres, hybrid ultrathin electrospun materials containing commercial ceramic nanoparticles of different nature have been recently developed. Reinforced hybrid nanostructures are of interest in coatings, packaging, encapsulation and other applications.

Active and Antimicrobial Packaging

Active packaging is defined as packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system [12]. Antimicrobial packaging is a form of active packaging. It involves use of active compounds such as oxygen scavengers, ethylene scavengers, moisture absorbers, natural antimicrobial agents, etc. [13]. The electrospinning process takes place at ambient conditions, and hence the electrospun fibers are more suitable for encapsulating thermally labile active agents as compared to other fibre producing techniques such as conventional melt spinning process and spray drying. Surface area of electrospun fibres is generally higher providing the additional advantage incorporating bioactive substances.

Water Absorbing Pad

When a polymer solution containing elastomer and superabsorbent is electrospun, nanofibres are produced in which the superabsorbent particles are held in place with nanoscale elastic fibers. Structured hydrogels are formed by nanofibres on fluid absorption. Increase in the weight gain due to water absorption may range from 400% to 5000% [14]. It was reported that composite fibre mat of polyvinyl alcohol and silica with a diameter of 200–400 nm can be obtained by electrospinning. With increase in silica content, arrangement of fibres changed from semi-crystalline to amorphous thus showing better swelling properties [15].

Antimicrobial Structures

In a study, active component such as allyl isothiocyanate (AITC) was formed into electrospun fibres using soy protein and polylactic acid possessing smooth morphology with diameters ranging from 200 nm to 2 μ m. AITC was protected from evaporation by incorporating cyclodextrin in fibre forming solution. AITC release from electrospun fibers was triggered by the presence of moisture and these electrospun fibres appeared to be a promising carrier for antimicrobial compound in active packaging applications [16]. Similarly, in another application, gallic acid was used as active compound. Gallic acid

disrupts the cell peptidoglycan and/or disintegrates the outer membrane of the bacteria through the chelation of divalent cations [17]. Micron-sized electrospun fibre mats of zein loaded with gallic acid acts as novel active packaging materials showing antibacterial activity towards both *Staphylococcus aureus* and *Escherichia coli* through a significant log reduction in their count [18]. Antimicrobial nanostructure has been incorporated in food packaging by electrospinning producing composite chitosan-ZnO nanofibres [19]. The minimum inhibitory concentration (MIC) of the composite nanofibres against *E. coli* and *Candida albicans* was 110 μ g/ml and 160 μ g/ml, respectively [20].

The presence of nano-ZnO in the nanofibres contributed to the antimicrobial activity of chitosan due to the adherence of nanofibres to cell membranes through electrostatic attraction which leads to denaturation of proteins and permeability changes in microbial cell membranes. Antimicrobial nanofibres of polylactic acid [21] and cyclodextrin obtained using electrospinning were having wider inhibition zones of *E. coli* and *S. aureus* [22]. It was reported that blending of zein (corn protein) with chitosan, a natural antimicrobial agent yields water insoluble fiber mats on being electrospun and this fibrous mat possessed efficient biocide properties [23].

Gas Leak Indicators or Sensors

Sensor is a device or an indicator, which detects or measures an attribute and records, indicates, or otherwise responds to it. The remarkable specific surface area and high porosity makes electrospun nanomaterials as highly attractive for the production of ultrasensitive sensors. Nanofibres fabricated through electrospinning have specific surface area considerably more than that of flat films, making them excellent candidates for potential applications in sensors. The fine structure of electrospun fibers proves to be an excellent candidate instead of the widely used solid flat films to further increase the sensor sensitivity [24, 25]. Modified atmosphere packaging (MAP) is an important packaging intervention in extending the shelf life of perishable dairy and food products. The technique involves

modifying the ambient atmosphere surrounding the product, which usually ends up with reducing oxygen and increasing carbon dioxide and/or nitrogen. Shelf life of several dairy products such as cheese, *paneer*, *burfi*, *peda*, etc. has been found to extend by the application of MAP. However, the success of the MAP largely depends on the integrity of the package. Introduction of gas leakage indicators into a MA packaged product brings confidence to the prospective buyers or consumers and enhances the brand image of a dairy products manufacturer. Several gas indicators are available in the global market. However, if an electrospun material is used as gas indicators, it is expected to enhance the sensitivity and selectivity of a particular gas thereby helping in detecting the minute presence of a selected gas; for example, oxygen. The polymer is electrospun to produce nanofibres, which can be used as nanosensors for detecting gas leakage indirectly giving an indication of pack integrity.

CONCLUSION

Electrospinning technology is used to form thin structures for different end uses with less energy and less chemicals to deliver the products with unique characteristics. Since it is only a beginning of the use of electrospun structures in packaging applications, huge potential exists for its use in Indian dairy and food industry. However, advancements in this field would require interdisciplinary efforts to enhance the theoretical understanding of the process to reap the benefits.

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