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ELECTROSPINNING – 100 YEARS OF INVESTIGATIONS AND STILL OPEN QUESTIONS OF WEB STRUCTURE ESTIMINATION

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Abstract:

The article presents an overview of electrospinning process development from the first investigations in the field of behaviour of liquids in an electrostatic field to the electrospinning methods and investigations in the 21st century. The article presents the history of electrospinning process development, the main problems that are solved, and also indicates the gaps in the field of standardisation of nanofibrous web structure measurement and estimation. There are a lot of works in which authors analyse influences of various parameters on the electrospinning process or on the structure of electrospun web, whereas the majority of them do not analyse the quality of structure using mathematical criteria. Such a situation leads to different conclusions and makes it impossible to compare various works by different authors. Despite numerous studies in electrospinning, investigations in the electrospun nanofibrous web estimation are not sufficient. Until now, a unique standard method for measuring and estimating the fibre diameter and web porosity has not been developed. The necessity of such a method and standards is obvious, and the lack of such a standard could have a negative influence on the electrospun product introduction into the market.

Keywords:

electrospinning, nanofibres, structure of web.

1. Introduction

The process of using electrostatic forces to form synthetic fibres has been known for more than 100 years. This process, known as electrospinning, uses a high-voltage source to inject charge of a certain polarity into a polymer solution or melt, which is then accelerated toward a collector of opposite polarity. As the electrostatic attraction between the oppositely charged liquid and collector and the electrostatic repulsions between like charges in the liquid become stronger, the leading edge of the solution changes from a rounded meniscus toa cone (the Taylor cone). Fibres produced using this process typically have diameters in the order of a few micrometers down to the tens of nanometers. The capacity to easily produce materials at this biological size scale has created a renewed interest in electrospinning for applications in tissue engineering and drug delivery [1].

The investigations in electrospinning process development have become very intensive in the past decades and a lot of papers have been published about the development of technology of electrospinning, influence of some parameters on electrospinning, possibilities to electrospun nanofibrous web from various polymers as well from the blends and with additional functional nano- or microparticles. Unfortunately, despite the numerous investigations, a unique standardised method of electrospun web structure estimation has not yet been created, and various researchers use their own methods for structure description and estimation. It is a big gap for electrospinning science as it is impossible to compare the results obtained by different researchers.

The goal of this article is to overview the history of electrospinning process development from the first investigations in the field of behaviour of liquids in electrostatic field, to analyse the present situation in the field of electrospun web structure estimation and to highlight the main problems that are necessary to solve for creating a unique method of electrospun web structure estimation by which various researchers could have a possibility to analyse and to compare various results obtained by various researchers. The literature contains several definitions of nanofibres, but there is no single opinion. According to the official definition of nanoparticles, the name of nanofibres can be only used for fibres whose diameter is lesser than 100 nm; however, in different sources, various fibres, even the ones till 1 µm, are named as nanofibres. This question is still open and needs additional discussion.

2. Development of electrospinning process

Although the study of electrospinning process began only in the 20th century, the first record of the behaviour of magnetic and electrostatic phenomena appeared at the end of the 16th century when English scientist Gilbert described the influence of electric amber on the shape of a water droplet. He noticed that having duly elevated amber to approach the water drop, the latter loses the shape of the hemisphere and acquires a cone shape [2]. This was the first entry close to the electrospinning process when the liquid body changes its shape when exposed to an external electrostatic field.

After Gilbert's publication of the amber phenomenon, various experiments close to the electrospinning process were performed by English scientist Hooke and German scientist Bose [3]. The latter, in 1745, described aerosols caused by drops of fluid using high electrical potential. In 1749, French scientist Nollet described the fracture of an electric water stream [4]. On the basis of literature, it is likely that the first electrospinning experiments were performed in an electric field based on tests with fluids.

More significant work related to electrospinning was done by scientist Strutt, better known as Rayleigh. In 1882, he calculated the critical load, during which an insulated water drop of a certain radius became unstable. He confirmed the insights of Plateau's work by publishing the theoretical model for breaking the strain, experimentally showing how, when using stroboscopic lighting, the fluid trickles into droplets after its length exceeds the perimeter. This scientist also sought to explain the phenomenon that the electric charge can increase the stability of the rising water flow and the fact that the charge at a critical level is less stable. Rayleigh described the amount of charge required for droplet deformation [5-8].

The first electrospinning device with three types of indirectly charged spinning heads was patented by Cooley in 1900 [9]. The scientist analysed the precipitation of a viscous polymer solution on a positively charged electrode located next to a negatively charged electrode. In 1902, Cooley patented an electrospinning device that used auxiliary electrodes, which, in the course of the electric spin, formed a trick to the rotating collector [10]. Soon after Cooley, Morton analysed the possibilities of formation of thin filaments and in 1902; he patented the needle electrically spinning method that formed thin strands [11].

Further research on the electrospinning process was carried out by scientist Zeleny. One of his first discoveries was an electroscope to measure electric charge. After many studies on the electrical discharge, Zeleny published a paper on fluid droplet behaviour at the ends of thin metal tubes. In his work, he noted that the positive polarity of the discharge has the tendency to oxidise the ends of the steel needles more than the negative polarity. He also emphasised that the sharp ends require higher discharge stress than a cylindrical electrode of equal diameter. This scientist succeeded in creating a needle/capillary apparatus for investigating the emission of electricity into liquids. He experimented with fluids using a hemispherical droplet at the end of the tube and said that high tension would deform the droplet shape. The model of the electric spray device developed by Zeleny has been used up to now with some improvements [3, 12, 13]. A bit later, Hagiwara published investigations of silk and artificial fibers. He used electricity to orient the molecular structure of the colloidal fluid. Hagiwara caused a high voltage in the polymeric solution to reconstitute the components of the solution and maintain such a structure until the end of the process [14].

Probably, the greatest contribution to the development of electrospinning process in the 20th century was introduced by Formhals. In his first work, Formhals described an electrospinning machine with a rotating toothed shaft immersed in a polymeric solution bath. The operation of this device was based on the fact that the polymer solution dissolved in the polymeric strands only in the high electric field, resulting in the toothed shaft being connected to the voltage converter. As the voltage increases, the polymeric solution on the toothpick of the wetted shaft is forced to break away from the rotating disk, and when the polymeric solution is formed, the latter enters the assembly disc. The improved electrospinning device was successfully patented in 1934 [15]. One year later, he patented the electrospinning device that allowed the formation of shorter fibres [16, 17]. In his other patents, Formhals announced not only the fabrication of artificial filaments by electrostatic means but also the device for forming these threads. He also patented a machine that controlled the formation of polymeric filaments when controlling the electric field, whilst the latter were in an electric field. This scientist made a lot of effort to invent devices that could form the fibre suitable for use [18-20].

The first spinning method adopted by Formhals had some technical disadvantages. It was difficult to completely dry the fibres after spinning because of the short distance between the spinning and collection zones, which resulted in a less aggregated web structure. Subsequently, in 1940, Formhals patented another method for producing composite fibre webs from multiple polymer and fibre substrates by electrostatically spinning polymer fibres on a moving base substrate [21]. Another consequence of incomplete solvent evaporation was that the fibres tended to stick to the collector as well as to each other, making removal problematic. Thus, in the second patent, Formhals detailed a new process in which a greater distance was used between the spinning and collecting sites, thus alleviating many of the problems observed with his earlier apparatus. In his second patent, Formhals also described the use of multiple nozzles for the simultaneous spinning of a number of fibres from the same polymer solution as well as a means to direct the fibre jets toward the collector. In 1940, Formhals patented a new process in which a polymer solution was directly electrospun onto a moving base thread to generate composite fibres.

The studies involving electrospinning in 1936–1939 were also carried out by Norton, who in 1936 first patented the method of filament formation from a polymer melt. The Norton patent describes the method of spinning from a polymer melt using an electrostatic field and air flow [22]. In 1939, Nathalie D. Rozenblum and Igor V. Petryanov-Sokolov developed filters using electrospinning techniques fabricated. A Petryanov filter is a type of filtering cloth that is used for fine and superfine cleaning of air and other gases from fine aerosols [23]. In 1952, Vonnegut and Neubauer formed a droplet of a very small diameter from a polymeric solution. Three years later, similar studies were done by Drozin [24, 25]. A very significant study of the evolution of the electrospinning process was made by

Taylor, who in 1964, mathematically modelled the shape of a droplet affected by an electric field. This characteristic drop form is now called the Taylor cone. Taylor formulated the spherical fluid droplet for the electrostatic field [26]. During 1971, Baumgarten [27] succeeded in the formation of an ultra-small diameter acrylic fibre with electrical forces. In 1981, Larrond and Manley constructed an electric melt spinning device, in which the static weight was directed to the piston acting in such a way that a droplet formed at the tip of the needle from the polymer mold and droplet formed by the electrostatic forces [28]. At the beginning of the 1990s, several research groups (one of them represented by Reneker) showed that a large number of different organic polymers can be screwed into nanofibres [29].

Significant development of electrospinning process was made in the Czech Republic in 2004 when a group of scientists led by Jirsak developed and patented an electrospinning device with a rotating earthed electrode, Nanospider TM [30]. Nanospider™ technology is a patented, needle-free, high-voltage, free liquid surface electrospinning process. The technology is based on the discovery that it is possible to create Taylor cones and the subsequent flow of material not only from the tip of a capillary but also from a thin film of a polymer solution. The technology enabled Elmarco to build industrial scale production equipment without nozzles, needles or spinnerets. Nanospider™ technology allows the production of nanofibres from polymers solved in water, acids or bipolar solvents and is suitable for the production of organic high-quality fibres. This versatile technology is easily adapted to a variety of process parameters for the optimization of the specific properties of the produced nanofibres [31, 32].

Since 1995, there have been further theoretical developments of the driving mechanisms of the electrospinning process. Reznik et al. described the shape of the Taylor cone and the subsequent ejection of a fluid jet [33]. Hohman et al. investigated the relative growth rates of the numerous proposed instabilities in an electrically forced jet once in flight [34] and managed to describe the most important instability to the electrospinning process, the bending (whipping) instability. Thanks to the aforementioned technology, strands can be made of a variety of polymeric materials, such as synthetic polymers and natural proteins [35, 36]. A nanofibre material is characterised by rapid release of embedded polymer into the first test minutes [37, 38].

Electrospinning is currently the only technique that allows the fabrication of continuous fibres with diameters down to a few nanometers. The method can be applied to synthetic and natural polymers, polymer alloys and polymers loaded with chromophores, nanoparticles or active agents, as well as to metals and ceramics. Fibres with complex architectures, such as core–shell fibres or hollow fibres, can be produced by special electrospinning methods. It is also possible to produce structures ranging from single fibres to ordered arrangements of fibres [39, 40].

Natural polymers – such as silk fibroin, chitosan, hyaluronic acid, gelatin, fibrinogen, collagen – are the most widely used biomaterials in tissue engineering, because they have excellent biological, physical and chemical properties. In many cases, synthetic polymers are superior to natural ones, because their properties can be suitably modified to obtain specific properties such as the desired mechanical properties and the desired degree of degradation. The most commonly used biomedical applications in synthetic polymers are biodegradable hydrophobic polyester, such as polyglycolide (PGA), polylactide (PLA) and poly (ε-caprolactone) (PCL). Various biodegradable polymers such as PCL, PLA, PGA, polyurethane (PU) and copolymer polylactide-polyvinylpyrrolidone, are used in the manufacture of bone tissue engineering, cardiac implants, wound dressings and artificial blood vessels. co-glycolide (PLGA) and copolymer poly L-lactide-co-ε-caprolactone (P (LLA-CL)) [39].

It is known that the structure of nano- and microgenetic coatings is influenced by several technological parameters: applied voltage, polymer velocity, the shape of the electrodes, the distance between electrodes and capillaryecollector distance, and various authors have analysed the influence of the presented parameters on the electrospinning process and electrospun web [40-44]. During the papers' review, it was found that the authors' opinions on the influence of technological parameters on the structure and diameter of the formed fibres are often not the same. The choice of the fibre diameter calculation method has a great influence on the results of the research. It has been determined that authors do not always indicate all the parameters that might influence the results of the research. In the analysis of the influence of technological parameters, it can be seen that only some authors analyse how the diameter is distributed and the distributions obtained are compared with the distributions known in mathematics, but do not substantiate the choice. It can be stated that the analysis of the fibre diameter distribution is very important in assessing the influence of technological parameters on the structure of the formed mat [45-52].

Electrospinning from polymer solutions or melts is an effective and direct technique for producing nanofibres or webs from nanofibres. The basic direction of the development of the world textile industry concerns an increase in the production of multifunctional hightech or smart fabrics designed for various practical applications. The manufacturing processes developed and used to make such fabrics are more and more frequently based on nanotechnologies that create splendid prospects for significant optimisation of the performance properties of textiles as well as for the development of new types of fabrics for new application areas. The nanomaterials generated using this technology have a large surface area and are highly porous, making them very useful for many applications in diverse fields such as healthcare, biotechnology, environmental engineering, defence and security [53]. The special properties of nanofibres make them suitable for a wide range of applications, from medical to consumer products and industrial to high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, fuel cells and information technologies. [54-58]. Owing to that the investigations in electrospinning are very popular and a lot of papers are published every year. In Figure 1, the diagram of number of papers published in the sources cited in the Clarivate Analytics (former Thomson Reuters or ISI) Web of Science databasis is presented.

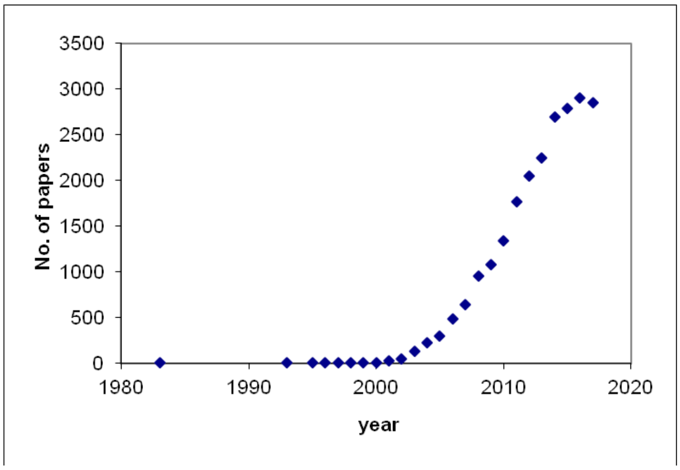

Figure 1. Diagram of number of papers published in the sources cited in the Clarivate Analytics Web of Science databasis

As is seen from Figure 1, the number of papers rose exponentially until 2014, whilst in the past three years, the number of papers stabilised and even more, in 2017, this number slightly decreased. Unfortunately, only very few papers are focused on the nanofibrous web structure estimation.

3. Nanofibrous web structure estimation

In electrospining, a web of nanofibres usually consists of nanofibres of different diameters. There is no single opinion about the reasons for such phenomena as the distribution of the nanofibre diameter is also very sophisticated. An analysis of various works shows that the distributions of the nanofibre diameter are always different and usually not close to a normal distribution. Thus it is very difficult to compare average values when the dispersions of diameters are different. The main problem is that the measurements of the diameter are distributed in an unclear distribution and characterising webs mathematically and evaluating the shape of the distribution obtained are not easy [59, 60]. The different thickness of fibres influences the structure of the web and herewith the end-use properties of such kind of nanomaterial [61, 62].

Analysing the papers, it was found that the authors sometimes compare the distribution of fibre diameters formed with laws well known in mathematics. In some cases, the distributions are similar to logarithmic distributions, and in such cases, the authors describe the distribution of the fibres in a logarithmic distribution [63]. As the diameter of the filaments formed during electrospinning does not depend on time, this distribution should not be used to describe the fibres diameter – this distribution does not have a physical sense. Other authors describe the empirical distribution formed by the normal distribution [60, 64]. From the material presented in papers, it can be seen that only some of them are similar to normal distributions, but other empirical distributions with multiple spikes are distributed in an incomprehensible distribution. Thus, in such cases, the usage of normal (Gaussian) distribution is not right. The authors do not explain why empirical distributions with multiple spikes are described by a normal distribution. Also, they do not analyse the reasons why frequencies often have multiple spikes. Such inadequate reasoning for results and inadequate analysis of empirical measurements results in inconsistencies in results and different choices [65]. From this, it can be concluded that without knowing the kind of distribution of fibres diameter, it is difficult to compare and analyse the influence of individual parameters on the formed nanofibrous web [66, 67].

Some authors argue that the increase in voltage does not have a significant effect on the diameter of the fibre but has a significant influence on the structure, so increasing the tension produces more clogged strands [68]. Other authors came to the conclusion that increasing the tension increases the average diameter of the formed nanofibres [69, 70]. The discrepancies were found and analysed by the influence of distance on the structure of nanofibrous web [71, 72]. There is no uniform view on the influence of temperature and relative humidity on the structure of the ionic coating [73]. It may be affected by inadequate analysis of the structure or failure to provide all the factors that could influence it.

Probably, the mismatches of the results occur because there is no common methodology for the characterisation of the structure of nanofibres [74]. Often the conclusions about the influence of parameters are presented based on the change in the average value of diameter, what is not right from the mathematical point of view in the case of different and sofisticated distributions. According to the changes in the average value, the conclusions of various authors are made about the influence of the parameters on the web structure, which can be one of the reasons for controversial results. The average diameter is very important for the estimation of the structure; however, only the average value cannot be used for the characterisation of the web [64, 72]. Owing to that an incorrect method of diameter estimation leads to not objective conclusions.

The authors rarely indicate the method of measuring the diameter of the fibres, how many fibres were measured to evaluate the structure, and how many measurements were made on the surface of the formed coating. The structure of electrospun webs are very often not uniform in the whole area [69, 75]. Analysis of papers has shown that authors sometimes evaluate the structure of the formed coating based on the data only from one or two SEM images [76]. This means that only one or two sites of a certain area are analysed, but this is not an objective method of structure evaluation because such an analysis does not take into account the unevenness of the entire structure of the resulting coating. However, in any case, it is necessary to evaluate the coverage of the entire area with the unevenness; therefore, the structure must be evaluated based on the different surface coating measurements and, more precisely, the influence of the parameters on the structure and diameter of the nanosized coatings.

Another parameter that characterises the structure of nanofibrous web is porosity. A very important parameter for describing porosity is the maximum value of the pore diameter in the surface of electrospun web. Such evaluation is especially important for nanofibrous webs of barrier application, which are used, for example, for antimicrobial protection. Preliminary analysis of webs shows a very big inequality of pore diameters in different places of nanowebs. Therefore, to measure only one or two SEM images is absolutelly not enough. There are a few methods for measuring the porosity such as conventional methods using apparent density and bulk density, image analysis and mercury porometer. On the other hand, the analysis of webs show a very big inequality of pore diameters in different places of nanowebs, but this inequality has not been fully investigated yet. However, until date, an accurate estimation of porosity in these grades of materials (nanofibre mat) is a difficult task.

Porosity is also very important if the electrically spiked nano-formed cells are used for cell growth or barrier properties [77-80]. In these cases, not only the maximum size of the pore but also all the distribution of pores size are important. Many authors describe in their work the porosity of the structure of the nanoweb, but the papers do not provide porosity estimation methods. The investigations in describing nanofibrous web porosity have not yet been published. So, the evaluation of the structure, and especially the complexible evaluation of porosity, is still an open question that needs to be solved in the future.

4. Conclusion

The electrospinning process was described more than 100 years ago and various researchers proposed various methods for fibre electrospinning. The interest in electrospinning especially rose at the end of the 20th century when the fibres in nanolevel were created. In the past decade, hundreds of papers have been published. On the other hand, the number of investigations and published papers is inadequate on the quantity of products containing the electrospun fibres in the market. One of the reasons of such a situation could be a very low capacity of electrospinning equipment and, consequently, the high cost of the product. Another reson could be the reliability of properties, especially barrier properties, of such materials. Despite the numerous studies in electrospinning, the investigations in the electrospun nanofibrous web estimation are not sufficient. So far, no unique standard method has been developed for fibre diameter measurements and estimation. One more sofisticated situation exists in nanofibrous web porosity estimation. There is no completed work or any proposed method in this area. This research field is open for new researchers, new investigations, new suggestions and new discussions.

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