Melt Electrospinning – Characteristics, Application Areas and Perspectives

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Abstract. Electrospinning is one of the most used processes in the production of nanofibers, due to its simplicity and versatility. This paper presents the current state of the melt electrospinning, which is less used than the solution electrospinning but which is the only way of electrospinning polymers with limited solubility and high electrical resistivity such as polyolefins. The advantages of melt electrospinning, as well as the constraints of this method, are reviewed, and the factors that influence the process are described. The paper are presented the main applicability domains of nanofibers obtained in this way and the prospects of future development.

1. Introduction
Nanotechnology, which is called the technologies of the future, is an interdisciplinary area of science and technology capable to produce materials having dimensions in the range of 0.1 to 100 nanometers [1-5]. These materials have very special features that are not found in bulk materials [6-10], such as high surface area, diverse surface functionality and high porosity, which make them usable in a wide variety of fields, from medicine to space technology, from environmental protection to telecommunications, from computer science to agriculture, from energy harvest and storage to nanomedicine [11-18].

Among nanomaterials, nanofibers, usually defined as fibres with diameter less than 1 μm, play a special role. Since nanofibres have only one nano scale dimension, while the others are at macroscopic one, it becomes possible to associate the benefits of nanostructures (high chemical and biological reactivity and electroactivity) with those of conventional solid membranes, such as comfortable manipulation and easy applicability. Nanofibre technology, which includes the synthesis, production and application of nanoscale fibres, is one of the foremost developments in nanotechnology [19-23]. Nanofibres can be obtained through electrospinning, phase separation, template synthesis, self-assembly or melt blowing [24-28]. For its simplicity, suitability for a variety of polymers and capacity to produce controlled sizes fibres with high surface to volume ratio, electrospinning is one of the most used nanofiber fabrication method. During the last few years, electrospinning has become a promising method for obtaining long and continuous fibers, with nanometer diameters, from a great variety of polymers. The applications range from performant filtering mediums or membranes, to driving sensors or systems, to medical textiles and medicines controlled-delivery to molecular photonics. In the electrospinning process, nanofibres are created by an electrically charged jet of polymer solution or
melt. The principle of electrospinning can be described as follows: by applying a high voltages electrostatic field (e.g. 10–50 kV) to a polymer solution or melt, the surface of the fluid stretches and forms first a conical shape, known as the Taylor cone. After that, when the electric voltage reaches a threshold value, the jet of charged liquid overcomes the surface tension and leaves the Taylor cone, being drawn to the collector of different potential and forming a nanofibre [29]. Hence, the stages of fibres electrospinning are: jet initiation, its extension and finally nanofibre formation [30]. In addition to the basic setup showed in figure 1, there are relatively many other approaches to the process.

2. Melt electrospinning - principles
The principle of the process is very much alike the principle of solution electrospinning: an electrical potential is applied between a polymer melt (which is supplied from a storage chamber and forced by a plunger or air pressure to a capillary, known as a spinneret) and an electrically conducting collector surface [31]. An example of a melt electrospinning setup is shown in Figure 1.

3. Particularities of the melt electrospinning process
Melt electrospinning has a number of advantages over solution electrospinning, mainly associated to the absence of solvent, which reduces cost, increases productivity [32] and makes the process more environmentally friendly [33]. In addition, in melt electrospinning, it is possible to transform into nanofibres polymers which cannot be dissolved, such as polyolefin or polyethylene terephthalate, or mixtures of polymers for which it is difficult to find a unique solvent for all the components [34]. Unlike solution electrospinning, where frequently a nonwoven fibrous mat is obtained, the melt electrospinning can produce filaments which can be used in knitting or weaving processes. In this case, the melt electrospinning process (known as melt electrospinning writing) uses a moving collector, which moves a translational movement sufficiently fast for the rectilinear deposition of the polymer jet [35]. Another beneficial property of melt electrospinning is that it produces highly uniform fibres with very little changes in the fibre diameter [36]. In addition to these advantages, there are difficulties arising from the particular equipment required and the high viscosity and low electrical conductivity of melt polymers. The special characteristics of the melt spinning make a difference in the way the process is influenced by the main parameters, compared to the filament in the solution.

3.1. Parameters influencing the melt electrospinning process
Even if the same main categories of influence factors (polymer characteristics and process parameters) are found in the melt electrospinning as well as in the solution electrospinning, the way they influence the electrospinning process knows some significant differences.

3.1.1. Polymer parameters. The main feature of the polymer melt that influences electrospinning is viscosity. As the viscosity of the melt is at least one order of magnitude greater than that of the polymer solutions, it is essential to reduce it. This is usually done by raising the temperature (without
degrading the polymer) or by adding additives such as cationic surfactants [37, 38], anionic tenside such as sodium oleate and salt [39]. Molecular weight of the polymer is another significant parameter related to the polymer melt, which influences the diameter of the electrospun nanofibres. When the molecular weight of the electrospun polymer is higher, the Melt flow index is lower and the diameter of the fibres is bigger. Because in the melt electrospinning the viscosity can not be controlled by adjusting the polymer / solvent ratio, like in the solution electrospinning, it is essential to choose a suitable molecular weight of the polymer to achieve a stable and reproducible electrospinning process [31]. It is believed that the optimal range of molecular weights for melt electrospinning is substantially lower than that characteristic of solution electrospinning. The process is also influenced by the stereoregularity of the polymer, the isotactic polymers producing finer fibres than the atactic ones [34], allegedly because side chain randomly placed on the polymer backbone affects the crystallization process [40]. The conductivity of the polymer melt decisively influences the stability of the extruded polymer jet. A too high conductivity determines the jet's instability, while a too small one will cause reduced electrostatic traction forces. It is considered that average conductivity values in the range of $10^{-6}$-$10^{-8}$ S / m prerequisites for a stable electrospinning process [41].

3.1.2. Process parameters. In what regards the processing parameters that influence the melt electrospinning process, it has been found that, in contrast to the solution electrospinning, there is a direct proportionality relationship between the electrospun nanofibre diameter and the melt polymer flow rate. The information referring to the effect of the applied voltage on the diameter of the fibres is inconsistent, but the general conclusion is that for each polymer there is an optimum voltage range [42-45]. The spinneret to collector distance is relatively smaller in melt electrospinning than in the solution process (usually 3 - 5 cm). This distance effects the cooling process of the polymer melt jet and the shape of the fibres. At smaller spinneret to collector distances flat fibres may appear, while larger distances influences the accurateness of depositing filaments on the collector in the melt electrospinning writing process.

3.2. Melt electrospinning set-ups

Besides the basic installation shown in Figure 1, various system configurations have been reported [43], showing variations especially in the melting polymer zone and in the melt polymer release zone. Heating system plays a significant role in whole melt electrospinning devices [47 - 49]. The melting of the polymer can be realised by heating the polymer chamber with circulating fluid, with electricity or directly with heated air (Figure 2 A-C). For polymers that are likely to suffer thermal degradation when stored for longer periods above their melting temperature, the classical melting zone was replaced by a laser melting zone, where monofilaments, rods of bundles are mechanically fed to reduce the heating time of the polymer [50-52] (Figure 2 D). The laser directed at the solid polymer acts both as jet initiation point as well as heating source.

Figure 2. Various polymer heating devices in melt electrospinning: (A) fluids circulating, (B) electrical heaters, (C) heated air, (D) converging lasers.

To bring the polymer melt to the spinneret various devices are used: screw extruder and mechanical feeding mechanisms (Figure 3 A), syringe pumps/plungers (Figure 3 B) or air pressure (Figure 3 C).
Figure 3. Various delivery of the polymer melt to the spinneret systems: (A) screw extruders, (B) in-line mechanical plungers, (C) air pressure.

The collectors can be stationary, x–y stage or rotating (Figure 4). Generally, the collector is made of stainless steel, aluminum or copper (Cu) plate. Glass collectors or plates covered in aluminum foil are used as well [53-55].

3.3. Future developments in the melt electrospinning process

The study of the melt electrospinning is still at the beginning, and the huge potential of nanofibers obtained this way is just beginning to be discovered. It is expected that melt electrospinning offers solutions to some of the problems restraining the industrial implementation of solution electrospinning. The special features of nanofibers obtained by melt electrospinning are mainly appropriate for biomedical engineering, and is likely to be used within new treatments and innovative approaches such as the encapsulation of functional materials within nanofibres. Other domains of future applicability are sensors, filtration, and protective textile materials.

4. Conclusions

The melt electrospinning of polymer nanofibers, as it is done in the absence of solvents, offers important benefits such as: transformation into nanofibers of polymers with limited solubility, exclusion of environmental problems associated with the use of solvents, uncomplicated material preparation, cost reduction, fast process. The paper reviews the main factors influencing the melt
electrospinning, the particularities of the melt electrospinning devices and the perspectives of the process.

5. References
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