

The Influence of Polymer Solution on the Properties of Electrospun 3D Nanostructures

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Abstract. The remarkable versatility of electrospinning is the result of the fact that many factors influence the process results. The characteristics of the electrospun nanofibres depend crucially, besides technological parameters, on the nature of the polymer solution. In the present article it is overviewed the way the properties of the polymer solution, such as concentration, viscosity, conductivity, surface tension, volatility characteristics of the used solvent, influence the main features of the obtained nanofibres.

1. Introduction

Electrospinning is the cheapest and the most straightforward way to produce extremely thin polymer fibers with diameters down to the nanometer scale, which have very high surface area. In electrospinning the mechanical force that is applied to the end of a jet in conventional fiber spinning is substituted by the electric body force that acts on elements of charged fluid [1-5]. A schematic diagram of the electrospinning process is shown in Figure 1.

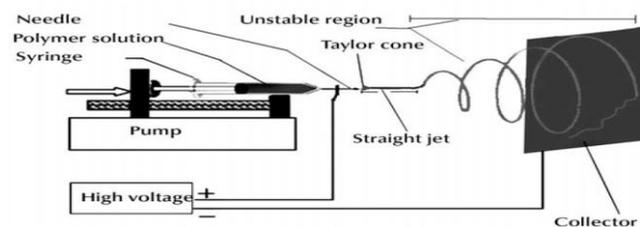


Figure 1. Electrospinning setup [1].

A significant quality of the electrospinning process is its versatility that allows the production of nanofibers of various compositions with controlled structures and multiscale and multifunctional assembly possibilities. Using electrospinning process one can produce a large diversity of materials with enhanced and tuneable properties for a wide range of applications [6-10]. In the beginning, electrospinning has been exclusively applied on the production of nanofibers of natural and synthetic polymers and carbon, with applications in filtration, textile and biomedical systems [11-13], but in the last years this process was extended to fiber formation based also on metal oxides, metals, and composite/hybrid systems [14-17].

2. Main polymer solution characteristics that influence on the properties of electrospun nanofibers

2.1. Viscosity

The surface tension and viscoelastic properties of the polymer solution are among the key parameters of electrospinning process [18-20]. These characteristics can be controlled by appropriate choice of the polymer concentration, which determines whether the electrospinning process can take place and has a dominant effect on the fiber diameter, as well as its morphology [21, 22]. The viscosity of the solution is usually considered to be the dominant parameter which decides fiber diameter [23] and if the solutions will electrospin at all. The viscosity of the electrospun polymer solution should be situated within a properly delineated range, outside which electrospinning can not be realised. A too low viscosity may result in interruption of polymeric filaments and droplets of polymer (electrospray), while a too high viscosity makes it impossible to extrude the polymer. The minimum required viscosity threshold corresponds to a certain polymer concentration in the solution to be electrospun and varies depending on the molecular weight of the polymer and the nature of the used solvent. The importance of electrostatic viscosity of the polymer solution is illustrated in figure 2.

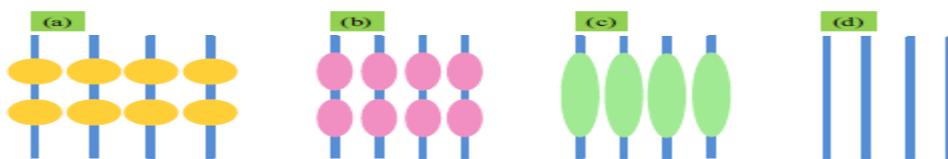


Figure 2. The viscosity increases from a) to d): a) drops; b) drops slightly elongated; c) elongated drop; d) nanofibers [24].

In general, a spinning solution with a viscosity of 1-20 poise values and values of surface tension of 35-55 dyn/cm² is considered to be a solution suitable for electrospinning. At viscosities of more than 20 poise, electrospinning is prevented because of polymer flow instability due to the high cohesion of the solution. When the solution viscosity is increased, the polymer beads are larger, the average distance between them is longer, and the diameter of the obtained fibers is increased. The formation of such beads occurs because the fluid flow breaks into

droplets when the viscosity of the spinning solution is less than 1 poise [25]. As the solution concentration increases, the shape of the beads changes from spherical to spindlelike [1]. The lower the polymer concentration, the smaller the diameter of the electrospun nanofibers, but the quantitative ratio between the concentration of the polymer solution and the diameter of obtained nanofibers is mostly variable.

Nevertheless, reducing the diameter of nanofibers by lowering the concentration of the polymer solution is limited by the possibility of processing the solution through electrospinning, as well as the possibility of reducing the diameter in post-processing treatments [26]. A change of the surface morphology of individual fibers, obtained by producing of pits, pores or protuberances on their surface or modifying the circular shape of their cross-section by regular or irregular patterning of the surface provides an alternative or complementary method to increase the surface area of the nanofibers [27].

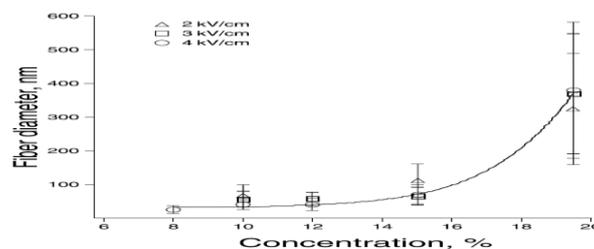


Figure 3. The relationship between fiber diameter and the polymer solution concentration at different values of the electric field [28].

The close relationship between the viscosity and the concentration of the polymer solution to be electrospun has been studied for polymers such as poly (lactic-co-glycolic acid) (PLGA) [29], polyethylene oxide (PEO) [30, 31], polyvinyl alcohol (PVA) [32-34], polymethyl methacrylate (PMMA) [35], polystyrene (PS) [36], poly-L-lactic acid (PLLA) [23], gelatine [28] and dextran [24]. A study on the relationship between viscosity and concentration on electrospinning of seven linear homopolymers of poly(methylmethacrylate) with different molecular weights using dimethylformamide (DMF) as solvent showed that the electrospinning of the polymethyl methacrylate (PMMA) of low molecular weight at concentrations less than six times bigger than the overlap concentration (concentration of polymer at which the viscosity of solution changes abruptly) only produced beads, while high molecular weight PMMA produced fibers with some beads at concentrations in this range [34].

An innovative approach to reduce the viscosity of the polymer solution is to use low-frequency vibration of the solution during the process [37, 38]. The vibration facilitates provisional untangling of the polymer chains by the disruption van der Waals interactions between the polymer chains, which leads to a reduction in the solution viscosity. The viscosity of a PMMA solution could be reduced by an order of magnitude when a vibration with a frequency of 300 rad/s was applied to the solution [37, 38]. The vibration of the tip of the capillary (about 400 kHz) during

electrospinning of a poly (butylene succinate) (PBS) / CHCl_3 solution led to the generation of nanofibers thinner in comparison with the situation in which no vibration were applied [39]. At higher concentrations of the polymer solution electrospinning can be realised only with the application of vibration. Another advantage of this technique is the possibility to electrospin suspensions and coagulated material which otherwise cannot be electrospun [27].

2.2. Conductivity

The electrospinning process fundamentally requires electrical charge transfer from the electrode to the polymer droplet located at the ending point of the injection needle, hence a minimum electrical conductivity in solution is essential to the electrospinning; solutions devoid of conductivity can not be electrospun.

The conductivity indicates the number of electric charges found on the surface of the polymer solution to be electrospun, and controls its tendency to form nanofibers and not nanodrops.

When dissolving a polymer in a solvent, the conductivity of the solution increases due to the availability of ionic species in the polymer (mostly being impurities or additives). However, with increasing concentration of the polymer in the solution, the electrical conductivity may decrease [10]. If the polymer itself has ionic capabilities of polyelectrolyte type, the conductivity of the solution will be much higher (compared to the solutions of the polymer without electric charges) and significantly depends on the concentration [28].

A correction of the lack of conductivity of the polymer solution can be obtained by adding electrolyte, when the increased number of electrical charge cause an increase in the elongation capacity of the solution, favouring the formation of smooth fibers, with smaller diameter [29].

Inorganic salts such as NaCl (0.01 M) [21, 30, 31] or ionic organic compounds such as pyridinium formate (PF) [10], palladium diacetate [32], triethylbenzyl ammonium chloride [33, 34] can be used to improve the conductivity of the polymer solution.

In this case the size of the ions affects the morphology of nanofibers; the obtained diameters are smaller as the size of the ions is smaller, as a result of their increased mobility, which leads to a higher tensile force of the jet of electrospun polymer, favouring the uniformity of the fibers and the reduction of the number of flaws [35].

2.3. Surface tension

The surface tension is the property of the liquid that shows the strong cohesiveness of the liquid molecules, indicating the dissimilarity of the phases at the interface [36].

The surface tension, which is strongly influenced by the nature of the solvent from the polymer solution, is a very important factor in electrospinning. This is why the correct selection of the solvent is critical not only to obtain a homogeneous solution of the polymer, but to obtain the right surface tension. Basically, if all the other conditions are set, the surface tension establishes the upper and lower limits of the range in which electrospinning can be achieved [37-42]. Lower surface tension of the spinning solution aids electrospinning to occur at lesser electric field

[1, 43-47]. In the absence of any electric field, the polymer solution is retained at the tip of the capillary by the surface tension of the liquid. When applying the electric field, the polymer jet is formed as a result of the action of the electric charges that overcome the surface tension of the solution, and therefore a decrease in the surface tension of the polymer solution induces instability to the jet and increases the breaking tendency of the extruded filament, with the formation of drops [48-53]. The surface tension can be adjusted by altering the polymer / solvent ratio in the electrospinning solution [54-60]. Another method of reducing the surface tension is to add surfactant to the solution, a procedure which ensures more uniformity to the fiber. However, not necessarily a lower surface tension of the solution will always be suitable for electrospinning [36, 61-65].

3. Conclusions

Nanofibers can be manufactured by interfacial polymerization and electrospinning, but electrospinning is the technique that offers a large versatility in what regards polymer compositions and the possibility to control the structure of the nanofibers.

This paper presents new research in the field electrospinning as a process used to produce nanofibers and offers a report on the main characteristics of the polymer solution that may affect the properties of the obtained nanofibers. The influence of viscosity, conductivity and surface tension is reviewed.

References

- [1] Hagi A K 2012 *Electrospinning of nanofibers in textiles* CRC Press, Boca Raton Finland
- [2] Calin M A, Khenoussi N, Schacher L, Adolphe D, Manea L R, Gradinaru I, Zetu I and Stratulat S 2013 *Mat. Plast.* **50** (4) 257
- [3] Scarlet R, Manea L R, Sandu I, Cramariuc B and Sandu A V 2012 *Rev. Chim.* **63** (8) 777
- [4] Scarlet R, Manea L R, Sandu I, Martinova L, Cramariuc O and Sandu I G 2012 *Rev. Chim.* **63** (7) 688
- [5] Manea L R, Scarlet R and Sandu I 2015 *Rev. Chim.* **66** (10) 1622
- [6] Cavaliere S 2016 *Electrospinning for advanced energy and environmental applications* (CRC Press, Boca Raton, Finland)
- [7] Popescu V, Manea L R and Popescu G 2009 *Management of Technological Changes* ed Rusu C. (Alexandroupolis, Greece, 3-5 September 2009) (Proceedings of the 6th International Conference on the Management of Technological Changes, Book 2) pp 769-772
- [8] Zhou W, Li Z, Zhang Q, Liu Y and Wei F 2007 *J. Nanosci. Nanotechnol.* **7** 2667
- [9] Manea L R, Hristian L, Leon A L and Popa A 2016 *IOP Conf. Series: Mater. Sci. Eng.* **145** 032006
- [10] Hristian L, Ostafe M M, Manea L R and Leon A L 2016 *IOP Conf. Series: Mater. Sci. Eng.* **145** 032004
- [11] Huang L, Nagapudi K., Apkarian R P and Chaikof EL 2001 *J Biomater Sci Polym Ed.* **12** 979
- [12] Frenot A and Chronakis I 2003 *Curr.pin. Colloid Interface Sci.* **8** 64
- [13] Hristian L, Ostafe M M, Manea L R and Leon A L 2016 *IOP Conf. Series:*

- Mater. Sci.Eng.* **145** 022014
- [14] Greiner A and Wendorff J H 2007 *Angew. Chem. Int. Ed. Engl.* **46** 5670
- [15] Manea L R, Scarlet R, Amariei N, Nechita E and Sandu I G 2015 *Rev. Chim.* **66** (4) 542
- [16] Asaftei I V, Sandu I G, Birsa L M, Manea L R and Earar K 2015 *Rev. Chim.* **66** (3) 336
- [17] Hristian L, Sandu A V, Manea L R, Tulbure E A and Earar K 2015 *Rev. Chim.* **66** (3) 342
- [18] Attout A, Yunus S and Bertrand P 2008 *Polymer eng. and science* **48** 1661
- [19] Ginestra P, Ceretti E and Fiorentino A 2016 *A. Proceedings of The Second CIRP Conference on Biomanufacturing* **49** 8
- [20] Demir M M, Yilgor I, Yilgor E and Erman B 2002 *Polymer* **43** 3303
- [21] Zong X H, Kim K, Fang D, Ran S F, Hsiao B S and Chu B 2002 *Polymer* **43** 4403
- [22] Jun Z, Hou H, Schaper A, Wendorff J H and Greiner A 2003 *e-Polym* **9** 1
- [23] Luzio A, Canesi EV, Bertarelli C and Caironi M 2014 *Materials* **7** 906
- [24] Abd Razak SI, Wahab I F, Fadil F, Dahli F, Khudzari A and Adeli H 2015 *Advances in Materials Science and Engineering* **2015** 1
- [25] Zong X H, Bien H, Chung C-Y, Yin L H, Fang D F, Hsiao B S, Chu B and Entcheva E 2005 *Biomaterials* **26** 5330
- [26] Andrady A L 2008 *Science and technology of polymer nanofibers* (John Wiley & Sons, Inc., Hoboken New Jersey)
- [27] Sukigara S, Gandhi M, Ayutsede J, Micklus M and Ko F 2003 *Polymer* **44** 5721
- [28] Ki C S, Baek D H, Gang K D, Lee K H, Um I C and Park Y H 2005 *Polymer* **46** 5094
- [29] Huang Z.-M, Zhang Y-Z, Kotaki M and Ramakrishna S 2003 *Compos. Sci.Technol.* **63** 2223
- [30] Son W K, Youk J H, Lee T S and Park W H 2004 *Polymer* **45** 2916
- [31] Ding B, Kim H Y, Lee S C, Shao C L, Lee D R, Park S J, Kwang G B and Choi C J 2002 *J Polym Sci B Polym Phys* **40** 1261
- [32] Lee J S, Choi KH, Ghim H D, Kim S S, Chun D H, Kim H Y and Lyoo W S, 2004 *J Appl Polym Sci.* **93** 1638
- [33] Kim J R., Choi S W, Jo S M, Lee W S and Kim B C 2005 *Journal of the Electrochemical Society* **152** A295
- [34] Gupta P, Elkins C, Long T E and Wilkes G L 2005 *Polymer* **46** 4799
- [35] Stanger J, Tucker N and Staiger M 2005 *Electrospinning* (Rapra Technology, Report 190)
- [36] Jiang H L, Fang D F, Hsiao B S, Chu B and Chen W L 2004 *Biomacromolecules* **5** 326
- [37] He J-H, Wan Y-Q and Yu J-Y 2004 *International Journal of Nonlinear Sciences and Numerical Simulation* **5** 253
- [38] Wan Y-Q, He J-H, Wu Y and Yu J-Y 2006 *Materials Letters* **60** 3296
- [39] Wan Y-Q, He J-H, Wu Y and Yu J-Y 2007 *International Journal of Electrospun Nanofibers and Applications* **1** 17
- [40] McKee M G, Hunley M T, Layman J M and Long T E 2006 *Macromolecules* **39** 575

- [41] Hagh A K and Zaikov G E 2011 *Development of nanotechnology in textiles* (Nova Science Publishers, Inc., New York)
- [42] Lee C H, Shin H J, Cho I H, Kang Y-M, Kim I A, Park K-D and Shin J-W 2005 *Biomaterials* **26** 1261
- [43] Wannatong L, Sirivat A and Supaphol P 2004 *Polymer International* **53** 1851
- [44] Yu J H, Fridrikh S V and Rutledge G C 2004 *Advanced Materials* **16** 1562
- [45] Zeng J, Xu X Y, Chen X S, Liang Q Z., Bian X C, Yang L X and Jing X B 2003 *Journal of Controlled Release* **92** 227
- [46] Choi J S, Lee S W, Jeong L, Bae S H, Min B C, Youk J H and Park W H 2004 *International Journal of Biological Macromolecules* **34** 249
- [47] Bhardwaj N, Kundu S C 2010 *Biotechnology Advances* **28** 325
- [48] Afshari M 2017 *Electrospun Nanofibers* (Woodhead Publishing Cambridge)
- [49] Li Z, Wang C 2013 *One-Dimensional nanostructures Electrospinning Technique and Unique Nanofibers* (Springer Berlin)
- [50] De Vrieze S, van Camp T, Nelvig A, Hagstrom B, Westbroek P and De Clerck K, 2009 *J Mater Sci* **44** 1357
- [51] Pillay V, Dott C, Choonara Y, Tyagi C, Tomar L, Kumar P, du Toit L and Ndesendo V 2013 *Hindawi Publishing Corporation, Journal of Nanomaterials* **2013** 1
- [52] Arumugam G K, Khan S and Heiden PA 2009 *Macromolecular Materials and Engineering* **294** 45
- [53] Manea L R, Berteau A P, Nechita E, Popescu C V and Sandu I 2016 *Rev.Chim.* **67** 8
- [54] Manea L R, Hristian L, Leon A L and Popa A 2016 *IOP Conf. Series: Mater. Sci. Eng.* **145** 032007
- [55] Maftei D, Asaftei I V, Sandu I, Manea L R, Birsa L M and Earar K 2015 *Rev. Chim.* **65** (5) 673
- [56] Manea L R, Cramariuc B, Caunii V and Sandu I 2015 *Mat. Plast.* **52** (1) 82
- [57] Popescu V, Manea L R and Amariei N 2009 *Mat. Plast.* **46** (1) 95
- [58] Manea L R, Danu M C and Sandu I 2015 *Rev. Chim.* **66** (6) 868
- [59] Leon A L, Manea L R, 2008 ITC&DC: 4th International Textile Clothing & Design Conference *Magic World of Textiles* ed Z Dragcevic (Dubrovnik, Croatia, 5-8 October 2008) (Faculty of Textile technology, University of Zagreb sections) E Book of Proceedings pp 803-806
- [60] Manea L R, Berteau A, Nechita E, Popescu C V and Sandu I 2016 *Rev. Chim. (Bucharest)* **67** (7) 1284
- [61] Hristian L, Ostafe M M, Manea L R, Sandu I G, Apostol L L and Sandu I 2016 *Rev. Chim. (Bucharest)* **67** (9) 1717
- [62] Manea L R, Chirita M, Hristian L and Sandu I 2016 *Mat. Plast.* **53** (3) 361
- [63] Popescu V, Radu C D and Manea L R 2010 *Industria Textila* **61** (1) 23
- [64] Popescu V, Manea L R, Curteza A and Vasluianu E 2011 *Tekstil* **60** (7) 306
- [65] Manea L R, Cramariuc B, Scarlet R, Cramariuc R, Sandu I and Popescu V 2015 *Mat. Plast.* **52** (2) 180