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Comparative Analysis of Electrospinning Methods for Producing Fibres and Materials with a Predicted Structure and Complex of Properties

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Abstract
Various industrial methods of electrospinning are considered. Experimental data of the results of electrospinning from solutions of chlorinated polyvinyl chloride, polyamide-6/66 and fluoroplastic F-42, obtained by various methods are presented.

Key words: *electrospinning, electrospun, nanofibres, nanospider, blowing-assisted electrospinning, electro-blowing, centrifugal electrospinning.*

Introduction

In recent years, there has been a growing trend of interest in the process of electrospinning, as evidenced by the increase in the number of publications and patents on this subject [1]. This is due to the possibility of processing practically any polymer into fibre, including biopolymers [6-8, 12, 14], as well as of the production of fibres with a diameter of less than 300 nm by electrospinning, which are due to the developed surface and small pore size in the material [9] providing high functional properties. In addition, the flexibility of the electrospinning process, the possibility of using a wide range of polymers and additives [2], the simplicity of the hardware design scheme at the laboratory research stage – all these components make it possible to widely use it for practical testing of the properties of synthesised substances [8], compositions of polymer solutions and fillers [10], as well as low molecular active substances and other modifiers [1-5, 15-21].

A significant part of the industrial appl ication of such materials is the filtration of gases [11, 13] and liquids [9], whose effectiveness is largely determined by the structure and properties of the fibrous web, which, in turn, depend on the method of electrospinning and its productivity [2, 4, 15, 20].

Since the 2000s, there has been an exponential increase in the number of publications and patents on the technology of electrospinning, which reflect information on various methods for implementing this process and on the applications of fibres [1-5, 15]. ***Figure 1*** shows the dynamics of link growth in the Web of Science scientific database for the search queries “electrospinning or electrospun” and “nanofibre or nanofibres”. It can be seen that the share of publications on the subject of electrospinning and the production of nanofibres by this method is more than half of all publications on nanofibres in general.

However, an insufficient number of review articles can be noted among the publications that provide a detailed analysis aimed at comparing the various electrospinning methods used on an industrial scale.

There are several electrospinning methods implemented in industry that can be conditionally divided into those using metering capillaries (electrocapillary, blowing-assisted electrospinning) and those using centrifugal electrospinning or nanospider [2, 16-20].

In the electrocapillary method (***Figure 2.a***), the formation of a jet is carried out on the surface of the capillary, and the number of jets is determined by the number of such capillaries [2, 4, 22-24]. The exception is specific modes with increased flow, in which the primary jet is divided into subsidiaries [25]. In the Nanospider ™ method (***Figure 2.b***), the number of jets on the surface of the string or cylinder is determined solely by the electrostatic field. The solution is applied to the string by dipping or spreading [26-28]. The extraction of fibres in both methods occurs only due to electrostatic forces.

In blowing-assisted electrospinning [2, 29-31] (***Figure 2.c***) and centrifugal electrospinning [2, 32, 33] (***Figure 2.d***), the spinning is carried out with the additional participation of high-speed flow air or centrifugal force acting on the solution. Due to this, the primary jet is crushed on the surface of the capillary or disk.

In Russia, for the production of microfibrous materials PF (Petryanov’s Filters®), the most famous is FPP-15-1.5, with the electrocapillary, electro- blowing and centrifugal methods also being used, while only the electrocapillary method is used to produce submicron fibres (analytical materials of the LFS-2 type) [2, 4].

As noted in many publications, where various methods of electrospinning are considered, the electro-blowing and centrifugal methods stand out as the most productive ones [2, 16-20]. However, almost all the experiments described were carried out using various electrospinning methods, with the use of different polymer-solvent systems at various concentrations [19, 20].

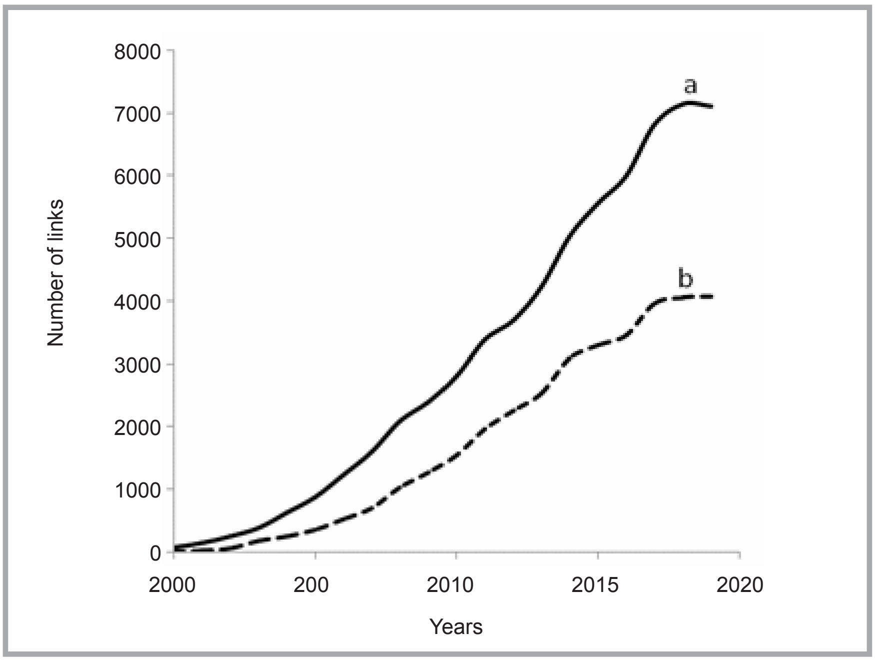

Figure 1. *Number of links in the Web of Science for search queries: a – nanofibre or nanofibres, b – electrospinning or electrospun.*

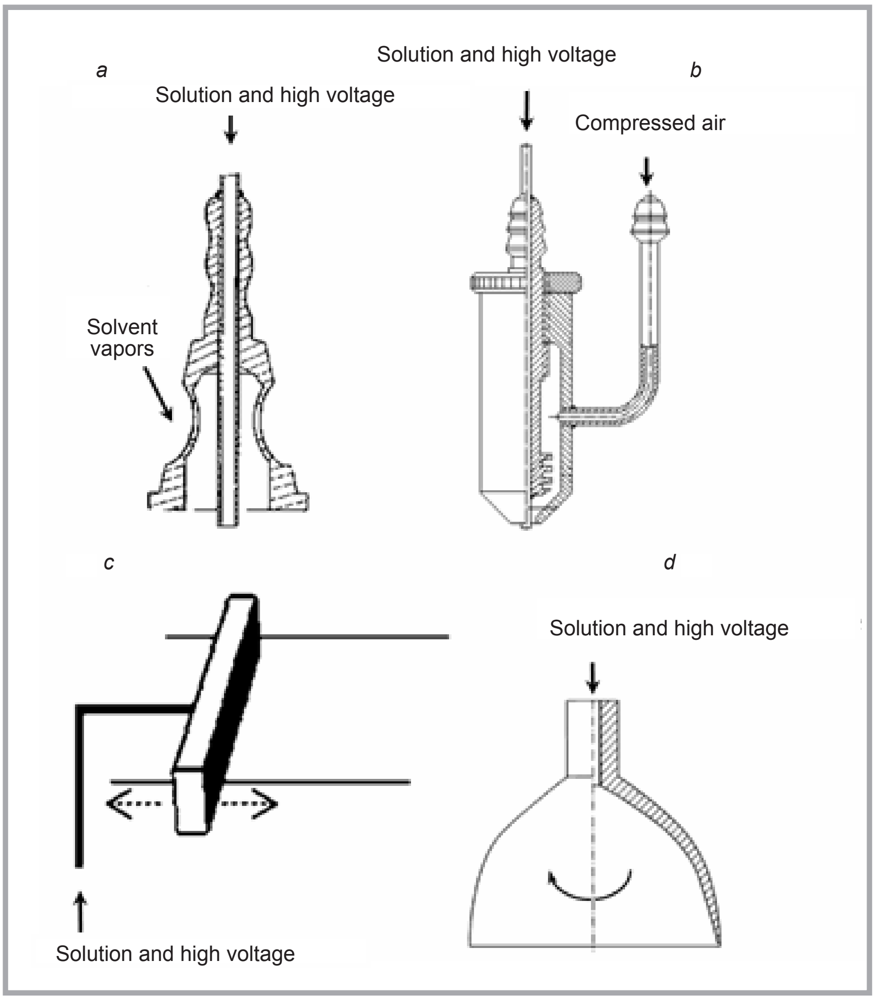

Figure 2. *Types of industrial methods of electrospinning: a – electrocapillary, b – electro-blowing, c nanospider, d – centrifugal. Reproduced with permission from [Filatov Yu. Budyka A., Kirichenko V. Electrospinning of micro- and nanofibres: fundamentals and applications in separation and filtration processes / – N. Y. : Begell House Inc. publ.]. Copyright Publisher, 2007.*

Therefore, the urgent task and purpose of this review is to systematise the knowledge about the possibilities of various electrospinning methods, compare the formulation and technological process parameters, carry out a multivariate assessment of the influence of the characteristics of the spinning solution (polymer-solvent pairs) on the structure and properties of the finished fibre, as well as select a specific electrospinning technology to obtain materials with specified structural characteristics and a specified set of properties.

Experimental

Materials

Polymers widely used for the production of nanofibres were selected as objects of study: chlorinated polyvinyl chloride (CPVC), molecular weight 55 kDa, manufactured by XiangSheng Plastic (China); polymethylmethacrylate (PMMA), molecular weight 160 kDa, manufactured by Dzerzhinsk Plexiglas JSC (Russia); polyamide-6/66 (PA), molecular weight 25 kDa, manufactured by Anid LLC (Russia); and fluoroplast (F-42), molecular weight 490 kDa, manufactured by LLC Ninth Element (Russia).

We used forming solutions of the above polymers in various solvent systems: a 10% PA-6/66 solution in a mixture of ethyl alcohol/propionic acid/acetic acid/water with an appropriate solvent ratio of 25: 20: 15: 40 mass; 6% solution of F-42 in dimethylformamide; 6% solution of F-42 in a mixture of dimethylformamide/toluene with a solvent ratio of 80:20 mass, respectively; 6% solution of F-42 in a mixture of dimethylformamide/ethyl acetate of 50:50 mass, respectively; and a mixture of 14% CPVC solution + 30% PMMA additive in a mixture of dimethylformamide/butyl acetate DMF/BA of 70:30 mass.

Methods

Three types of electrospinning were used in the work: capillary, centrifugal and electro-blowing. The capillary type apparatus was a SK-500I syringe dispenser with a 29G gauge needle (ISO14971: 2000 + A1: 2003, Shenzhen Shenke Medical Instrument Technical Development Co., China), where the minimum volumetric flow rate was 0.1-0.2 ml/h; the centrifugal the element was a polished steel disk with concave edges with a diameter of 100 mm, thickness of 0.5 mm, and disk rotation speed of

3000 rpm; air flow in the aerodynamic nozzle was about 30 l/min at a pressure of 0.1 MPa. A nanospider of the NS-LAB-500 series was used with a forming bath with a 4-string collector 15 cm long. A study of filtering aerosol particles at various linear flow rates was carried out on an Automated Filter Test Model 3160 TSI 3160 (USA).

Nanofibrous materials from the same polymer-solvent systems using various electrospinning methods were obtained in this work. A comparison was made for such parameters as fibre diameter, drawbacks and process performance.

Results and discussion

A comparison of electrospinning results by different methods for various process parameters can be made according to the following characteristics: average fibre diameter, nature of fibre diameter distribution, fibre porosity, average number of pores fibre and pore distribution in the fibre layer, as well as defectiveness. For fibrous materials used in filtration, a zero-defect quality is a very important characteristic, which is usually evaluated by visual analysis.

Defects during the electrospinning process can be divided into fibre defects and those in the finished material. The most common fibre defects are thickenings (***Figure 3.a***) in various configurations (spindle, ball), which are fragmentarily located in the structure of the canvas. The aggravation of such defects takes place during the transition of the process of electrospinning to that of electrospraying. This is accompanied by an increase in the size of thickenings, which can exceed the fibre diameter by more than 20 times. The reasons for the transition to electrospraying are: forming from solutions with a concentration below the crossover point, low conductivity of the solution, and/or a very high feed rate. Subsequently, such thickenings turn into drops of various sizes and, when reaching the surface of the fibrous material, form defects of two types: webs (***Figure 3.b***) and holes (***Figur 3.c***). Webs are formed from droplets of solutions containing volatile solvents (for example, acetone, ethyl acetate, etc.). Holes in the fibre layer are caused by droplets that do not have time to harden sufficiently. Defects in the form of drops can also form due to the heterogeneity of the polymer solution and the presence of gels, particles, etc.

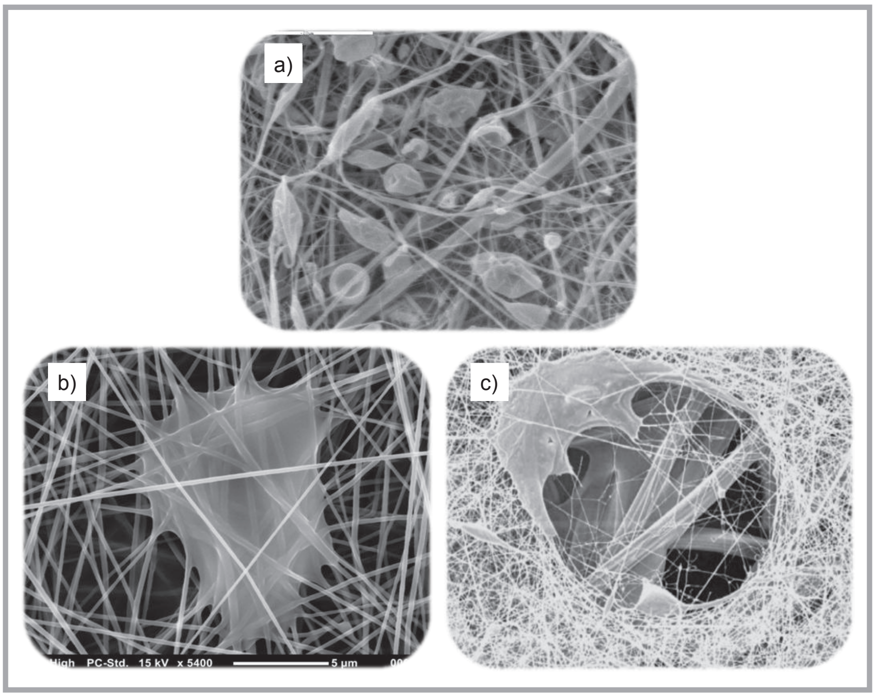

Figure 3. *Defects of nanofibre materials: a) thickening on fibres in the form of spindles, b) web from a drop, c) through penetration.*

The correct method for comparing various fibrous materials is to determine the average hydrodynamic diameter dr for them from the Fuchs-Stechkina hydrodynamic resistance formula [4] ***Equation (1)***.

Where, ΔP – resistance to air flow, Pa; μ is the viscosity of air; M is the surface density, g/m^2; v is the air velocity, m/s; r is the hydrodynamic radius of the fibre, m; ρ is the density of polymer fibres, g/cm^3; β is the packing density of fibres in the material; and $Kn = \lambda/r$ is the Knudsen number, where λ is the free length of air molecules, m.

The hydrodynamic diameter is almost always larger than the average optical diameter measured using an optical or electron microscopy, which is caused by defects in the value of surface density. The values of the average optical and hydrodynamic diameters can coincide only for zero-defect fibrous materials. Therefore, an increase in the hydrodynamic diameter reflects an increase in the number of defects well, for example, with an increase in the volumetric flow rate of the solution during electrospinning. In parallel, it is necessary to evaluate the average optical diameter of the fibres. Thus, calculation of the hydrodynamic diameter of the fibres can be used as a second method for assessing defectiveness.

Since forming solutions with a concentration above the crossover point and with optimal electrical conductivity were used in all experiments, the chosen method of electrospinning affected the defectiveness through the flow rate of a single jet solution.

Table 1 shows the results of the influence of the electrospinning methods using solutions of chlorinated polyvinyl chloride (with the addition of polymethylmethacrylate), polyamide-6/66 and fluoroplastic F-42 on the fibre diameter (dr), the presence of defects (visually determined) in the material and on the process productivity (Q). Using the F-42 fluoroplastic solution as an example, the influence of the type and composition of the solvent on these parameters was additionally analysed.

$$\Delta P = \frac{4\mu \cdot M \cdot v}{\rho \cdot r^2 \left[-0{,}5\ln\beta - 0{,}48 + 0{,}64\beta + 1{,}43(1-\beta) \cdot Kn\right]} \qquad (1)$$

Equation (1).

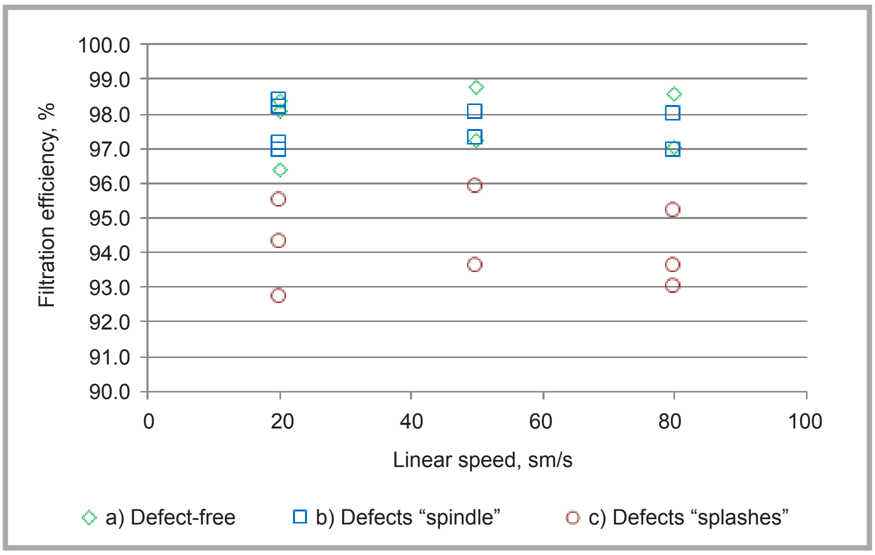

Figure 4. *Filtration efficiency of nanofibre materials with various types of defects: a) defect-free, b) defects in the form of spindles, c) defects in the form of splashes.*

The absence of defects in the materials obtained by the electrocapillary method was observed at minimum flow rates from the capillary.

The smallest fibre diameters were possessed by materials obtained using the nanospider, the volumetric flow rate of the solution is not regulated, but depends on the applied voltage and other factors, and is usually measured indirectly from the weight of the fibres deposited on the substrate for a certain time. The density of the jets per unit length of the nanospider electrode is approximately 5 to 10 pcs./cm. Thus, the average consumption of one jet is about 0.05-0.1 ml/h, which is lower than the minimum flow rate on the capillary. Therefore, the diameter of fibres for the nanospider is lower than or approximately equal to that of fibres at a minimum flow rate on the capillary. With an increase in the flow rate on the capillary, the fibre diameter increases 1.5-3 times from the minimum, after which an excess amount of the solution leads to the formation of defects on the fibre, as observed by micrographs and by the growth of the hydrodynamic diameter.

For F-42 solutions, the general tendency remains: an increase in the diameter and number of defects with an increase in the flow rate, while minimum fibre diameter values of 90 nm were obtained from a solution in the most volatile solvent – dimethylformamide.

It should be noted that the electrocapillary method is the only one in which it is possible to supply the solution into the jet above the optimal values until it is split into several jets at the edge of the capillary. It is also possible to lower the flow rate to a less than optimal value until the jet is broken off by field forces. It is necessary to understand that the word ‘optimal’ means at such a value of the flow rate that an electrostatic field would pull from the electro-blowing (for example, from a nanospider string). This makes this method the most manageable of all known.

Despite the minimal costs, fibres obtained by the electro-blowing method contain a significant number of defects in all cases. This, apparently, is associated with the wide distribution of values of the flow rate of single jets formed from the primary jet, which are fragmented by the air stream. In this case, for fibres with a diameter of less than 100 nmfibre and more than 300 nm, defects are formed. With a further increase in the flow rate through the nozzle, the hydrodynamic diameter also increases due to an increase in the number of defects and their size. In this case, the average optical diameter of the fibres remains practically unchanged. An increase in flow rates above a certain level results in droplets. It can be noted that the high-speed accompanying air flow dries out defects in flight.

The results of the centrifugal method are similar i.e. there is also the occurrence of a significant number of defects, the number and nature of which are not affected by a decrease in the flow rate of

Table 1. *Electrospinning results by various methods.*

Composition of forming solution	Capillary		Nanospider		Electro-blowing		Centrifugal	
	Q, ml/h	d_r, nm	Q, ml/h	d_r, nm	Q, ml/h	d_r, nm	Q, ml/h	d_r, nm
10% solution of PA-6/66 in a mixture of ethyl alcohol/ propionic acid/ acetic acid/water 25: 20: 15: 40 mass.	0.2	230	~ 12.0	160	3.0	360	–	–
	0.5	250			5.0	500		
	1.0	370			7.0	470		
6% solution of F-42 in a mixture of dimethylformamide/toluene 80:20 mass.	0.7	120	~ 10.0	100	7.0	140	50.0	160
	1.2	150			10.0	170		
	1.5	210			15.0	210		
6% solution of F-42 in dimethylformamide	0.1	90	~ 10.0	80	–	–	–	–
	0.3	110						
	0.6	120						
6% solution of F-42 in a mixture of dimethylformamide/ethyl acetate 50:50 mass.	0.3	230	~ 15.0	240	–	–	–	–
	0.7	300						
	3.0	420						
14% CPVC solution + 30% PMMA additive in a mixture of dimethylformamide/butyl acetate DMF/BA 70:30 mass.	0.2	150	~ 12.0	130	5.0	250	80.0	510
	0.5	180			7.0	300		
	1.0	240			10.0	450		

the solution. In addition, the solution begins to dry at the edge due to incomplete washing.

To assess the effect of defects on the filtering properties of materials, research of aerosol filtration particles DOP (dioctylphthalate) with a diameter of 0.4 µm at various linear flow rates (***Figure 4***) was performed. All materials had equal resistance to the air flow. Fibres obtained from chlorinated polyvinyl chloride were taken as test material: zero-defect, obtained on a nanospider (***Figure 5.a***); having spindle defects, obtained by the capillary method at a flow rate of 1 ml/h (***Figure 5.b***); and materials with defects in the form of splashes, obtained by the centrifugal method at a flow rate of 80 ml/h (***Figure 5.c***).

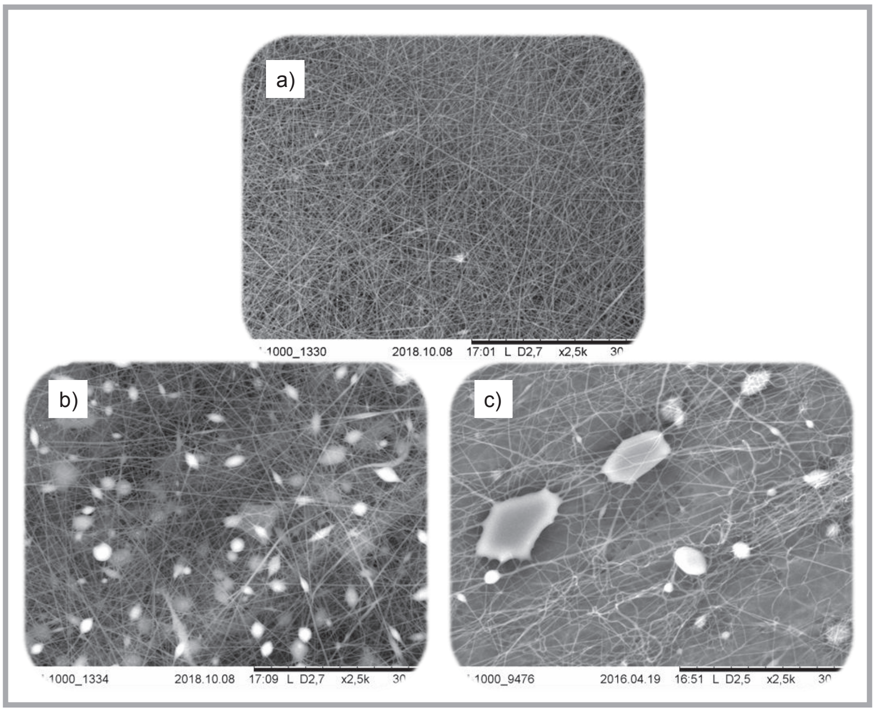

Figure 5. *Filtration efficiency of nanofibre materials with various types of defects: a) defect-free, b) defects in the form of spindles, c) defects in the form of splashes.*

The studies have shown that defects on spindle type fibres do not affect the filtering properties of nanofibre materials, and their presence can be neglected to achieve greater process performance (***Figure 4.b***). Defects in the form of splashes can degrade filter performance (***Figure 4.c***). Most splashes form webs in the layer of nanofibres, which affect only the total resistance to air flow, blocking the working area. However, some of them, falling on a layer of nanofibres, dissolve under themselves, making through holes, which are partially covered by subsequent layers of nanofibres. As a rule, the local surface density in such places is much lower, as a result of which there is a significant expansion of the filtration efficiency indicator and an increase in the particle breakthrough by 2-3 times in comparison to a defect-free material.

Conclusions

According to the studies, all electrospinning methods can be used to produce nanofibres. However, high-performance electro-blowing and centrifugal methods give a significant number of defects in the form of drops or thickenings. Due to the absence of through holes formed by drops and sufficient drying during settling, such defects can be neglected, for example, to create materials from mixtures of micro- and nanofibres for air filtration. These methods have a significant advantage in the performance and density of the jets in the forming space, while the forming elements are compact and can easily be set in motion for uniform fibre deposition.

The electrocapillary method, as the most controlled by the flow rate of the forming solution, allows the production of the least defective nanofibres. However, minimising the flow rate per capillary to obtain smaller fibres leads to a significant complication in the design and an increase in the number of capillaries.

The nanospider method, due to field strengths, depending on the viscosity and conductivity of the solution, allows to achieve the lowest costs per unit jet while self-regulating the distance between the jets. Such materials can be successfully used as liquid filters, since they have a minimal pore and zero- defect structure. However, the forming element in the form of a bath with a string collector or a string and a carriage is rather bulky and deprived of the possibility of movement. To increase uniformity, the sequential installation of a large number of such elements is required.

Thus, we can conclude that for each specific task for the further use of nanofibres, the productivity required and specific polymer-solvent system, the optimal method of electrospinning can be selected.

References

1. Arinstein A. *Electrospun Polymer Nanofiber*; Singapore: Jenny Stanford Publishing; 2017; 208 p.
2. Filatov Yu, Budyka A, Kirichenko V. *Electrospun Polymer Nanofiber*. New York: Begell House Inc publ.; 2007; 404 p.
3. Ramakrishna S, Fujihara K. *An Introduction to Electrospinning and Nanofibers*. Singapore: World Scientific Publishing Company; 2005, 396 p.
4. Druzhinin EA. Proizvodstvo i svoistva filtruyuschich materialov Petryanova iz ultratonkich polimernych volokon. Moscow: IzdAT; 2007, 280 p.
5. Asmatulu R, Khan WS. *Synthesis and Applications of Electrospun Nanofibers*. Amsterdam: Elsevier Science; 2018, 306 p.
6. Rylkova MV, Bokova ES, Kovalenko GM, Filatov IYu. Use of Water-Soluble Polymers for Electrospinning Processing. *Fibre Chemistry* 2012; 44, 3: 146-148.
7. Sonina AN, Uspenskii SA, Vikhoreva GA, Filatov YuN, Gal'braikh LS. Production of Nanofibre Materials from Chitosan by Electrospinning (Review). *Fibre Chemistry* 2011; 42, 6: 350-358.
8. Sokolov VV, Kil'deeva NR, Filatov YN. Preparation of Ultrathin Fibers from Copolyacrylmethacrylate Eudragit E Solutions by Electroforming. *Fibre Chemistry* 2012; 43, 6: 406-411.
9. Smul'skaya MA, Filatov YN. Optimization of Structure of Composite for Liquid Filtration Based on Membranes Produced by Electrospinning. *Fibre Chemistry* 2017; 49, 3: 195-199.

10. Gladyshev NF, Gladysheva TV, Suvorova YuA, Putin SB, Filatov YuN, Smulskaya MA, Filatov IYu, Rodaev VV, Ermakov AA. Poluchenie voloknistyh ftorpolimernyh kompozitov dlya pogloscheniya dioksida ugleroda metodom elektroformovaniya. *Kchiicheskaya Tehnologiya* 2014; 15, 2: 102-105.
11. Kapustin IA, Filatov IY, Filatov YN. Development of Production Technology for Non-Woven Filtering Materials for Monitoring Atmospheric Aerosols at RF Radionuclide Stations. *Fibre Chemistry* 2013; 44, 5: 299-303.
12. Ol'khov AA, Akatov VS, Prosvirin AA, Staroverova OV, Iordanskii AL, Filatov YN, Gol'dshtrakh MA. Implants for Reconstructive Surgery Based on Electrospun Poly(3-hydroxybutyrate) fibers. Fibre Chemistry 2017; 49, 3: 222-226.
13. Ekidin AA, Vasyanovich ME, Antonov KL, Markov DV, Markova ZhD, Kapustin IA, Filatov IY. Control of Aerosol and Gaseous Compounds of Iodine Isotopes in the Ventilation System of the IVV-2M Reactor Facility. H*ysics of Atomic Nuclei* 2018; 81, 10: 1494-1498.
14. Kovalenko GM, Bokova ES, Mirontseva VV, Filatov IY. Electrospun Fibrous Materials Made of Collagen and Chitin Derivatives. *Fibre Chemistry* 2017; 48, 6: 466-469.
15. Filatov IYu, Filatov YuN, Yakushkin MS. Elektroformovanie voloknistych materialov na osnove polimernych mikro- i nanovolokon. Istoriya, teoriya, technologiya, primenenie. *Vestnik MITCHT* 2008; 3, 5: 3-18.
16. Kozlov VA, Yakushkin MS, Филатов ЮН. Osobennosti apparaturnogo oformleniya prozessa elektroformovaniya polimernyh nano- и mikrovoloknistyh materialov. *Vestnik MITCHT* 2011; 6, 3: 28-33.
17. Zhou F-L, Gong R-H, Porat I. Mass Production of Nanofibre Assemblies by Electrostatic Spinning. *Polymer International* 2009; 58, 4: 331-342.
18. Niu H, Lin T. Fiber Generators in Needleless Electrospinning. *Journal of Nanomaterials* 2012; 1: 1-13.
19. Luo CJ, Stoyanov SD, Stride E, Pelan E, Edirisinghe M. Electrospinning Versus Fibre Production Methods: from Specifics to Technological Convergence. *Chemical Society Reviews* 2012; 41, 13: 4708.
20. Persano L, Camposeo A, Tekmen C, Pisignano D. Industrial Upscaling of Electrospinning and Applications of Polymer Nanofibers: a Review. Macromolecular Materials and Engineering 2013; 298, 5: 504-520.
21. Saleh Hudin HS, Mohamad EN, Mahadi WNL, Muhammad Afifi A. Multiple-Jet Electrospinning Methods for Nanofiber Processing: A Review. *Materials and Manufacturing Processes* 2017; 33, 5: 479-498.
22. Doshi J, Reneker DH. Electrospinning Process and Applications of Electrospun Fibers. *Journal of Electrostatics* 1995; 35, 2-3: 479-498.
23. Yamashita Y, Ko F, Miyake H, Higashiyama A. Establishment of Nanofiber Preparation Technique by Electrospinning. *FIBER* 2008; 64, 1: 24-28.
24. Yang Y, Jia Z, Li Q, Hou L, Liu J, Wang L, Zahn M. A Shield Ring Enhanced Equilateral Hexagon Distributed Multi-Needle Electrospinning Spinneret. *IEEE Transactions on Dielectrics and Electrical Insulation* 2010; 17, 5: 1592-1601.
25. Wu Y-K, Wang L, Fan J, Shou W, Liu Y. A Double-Switching Voltage: Controlling Multiple Jets in Electrospinning. *Materials Letters* 2018; 233: 359-362.
26. Petrik S, Maly M. Production Nozzle-Less Electrospinning Nanofiber Technology. *MRS Proceedings* 2009; 1, 5: 1240.
27. Forward Keith M, Rutledge Gregory C. Free Surface Electrospinning from a Wire Electrode. *Chemical Engineering Journal* 2012; 183, 5: 492-503.
28. Yalcinkaya F. Preparation of Various Nanofiber Layers Using Wire Electrospinning System. *Arabian Journal of Chemistry* 2016; 1: 134-135.
29. Um IC, Fang D, Hsiao BS, Okamoto A, Chu B. Electro-Spinning and Electro-Blowing of Hyaluronic Acid. *Biomacromolecules* 2004; 5, 4: 1428-1436.
30. Lin Y, Yao Y, Yang X, Wei N, Li X, Gong P, Wu D. Preparation of Poly(Ether Sulfone) Nanofibers by Gas-Jet/Electrospinning. *Journal of Applied Polymer Science* 2007; 107, 2: 909-917.
31. Hsiao H-Y, Huang C-M, Liu Y-Y, Kuo Y-C, Chen H. Effect of Air Blowing on the Morphology and Nanofiber Properties of Blowing-Assisted Electrospun Polycarbonates. *Journal of Applied Polymer Science* 2012; 124, 6: 4904-4914.
32. Weitz RT, Harnau L, Rauschenbach S, Burghard M, Kern K. P Polymer Nanofibers via Nozzle-Free Centrifugal Spinning. *Nano Letters* 2008; 8, 4: 1187-1191.
33. Engström J, Hagström B. Centrifugal Spinning of Nano-Fiber Webs – A Parameter Study of A Novel Spinning Process. *Nord. Text. J.* 2009; 1: 83-91.

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