THE INFLUENCE OF ELECTROSPINNING PARAMETERS ON THE MORPHOLOGICAL FEATURES OF PVDF FIBRES
INFLUENȚA PARAMETRILOR DE ELECTROFILARE ASUPRA CARACTERISTICILOR MORFOLOGICE ALE FIBRELOR DE PVDF

ANDRADA-ELENA ALECU [1], STEFANIA-ANDREEA GÎRJOABĂ [1], MIHAELA BEREGOI [2], SORIN-ION JINGA [1], CRISTINA BUSUIOC [1]*

[1] *University POLITEHNICA of Bucharest, RO-011061, Bucharest, Romania*
[2] *National Institute of Materials Physics, RO-077125, Măgurele, ROMANIA*

In this work, polyvinylidene fluoride was obtained in the form of one-dimensional structures with the help of electrospinning technique. Several types of precursor solutions were tested to find the optimal experimental conditions to produce smooth, continuous and beadless fibres, morphologically suitable for the development of piezoelectric scaffolds dedicated to tissue engineering applications. Thus, the influence of solvent type, polymer concentration, as well as electrospinning parameters (feeding rate, spinneret-collector distance, and applied voltage) was assessed and the best situation was the one with a 2:3 ratio between dimethylformamide and acetone, 20 % polymer concentration, 1 mL/h flow, 20 cm distance and 18 kV voltage. In the end, the fibres were loaded with barium titanate commercial particles, as first attempt to produce a piezoelectric composite with potential in the medical field.

În această lucrare, fluorura de poliviniliden a fost obținută sub formă de structuri unidimensionale cu ajutorul tehnicii electrofilării. Au fost testate mai multe tipuri de soluții precursoare pentru a găsi condițiile experimentale optime pentru a produce fibre netede, continue și fără „mărgele", potrivite din punct de vedere morfologic pentru dezvoltarea de scaffolduri piezoelectrice dedicate aplicațiilor de inginerie tisulară. Astfel, a fost evaluată influența tipului de solvent, a concentrației de polimer, precum și a parametrilor de electrofilare (debit de alimentare, distanță spinaretă-colector și tensiune aplicată) și cea mai bună situație a fost aceea cu un raport de 2:3 între dimetilformamidă și acetonă, 20 % concentrație de polimer, 1 mL/h debit, 20 cm distanță și 18 kV tensiune. În final, fibrele au fost încărcate cu particule comerciale de titanat de bariu, ca primă încercare de a produce un compozit piezoelectric cu potențial în domeniul medical.

Keywords: *polyvinylidene fluoride, barium titanate, fibres, electrospinning, morphology*

1.Introduction

The regeneration, repair and replacement of damaged tissues are intensively studied to elucidate the leading principles and mechanisms, and to find the appropriate substitute materials and efficient strategies, subsequently developing the field of tissue engineering [1]. Hence, a close collaboration between materials science and bioengineering fields is desired to design and manufacture improved medical devices or to establish personalized therapies [2, 3]. Many studies in the scientific literature propose a combination of cells taken from the human body with scaffolds made of biomaterials that are biocompatible, bioactive and bioresorbable, acting as a model to guide the growth of new tissues [4-7].

In the last few years, natural and synthetic biopolymers, such as polylactic acid (PLA) [8, 9], polyglycolic acid (PGA) [10,11], polycaprolactone (PCL) [12, 13], polyvinylidene fluoride (PVDF) [6, 14], chitosan [15, 16] and many others, were extensively used and have an important role in tissue engineering and regenerative medicine [17]. Polymeric fibres are one-dimensional structures adequate for the previously mentioned domains due to their ability to generate composite materials with superior properties, together with other phases (metals, ceramics, drugs etc.) [18].

Among these, PVDF ($(C_2H_2F_2)_n$) is a polymer with excellent mechanical strength [19, 20]. It is also considered one of the most suitable organic materials to study the polarizability of dielectric polymers; as features, PVDF exhibits good flexibility and processability, high thermal stability, exceptional chemical resistance, pyroelectric and piezoelectric properties, biocompatibility and even bioinertia [21, 22]. This is a semi-crystalline thermoplastic fluoropolymer displaying a structure in which most VDF units are joined head-to-tail, resulting in four possible conformations (α, β, γ, δ), from which β-phase is the desirable one from the piezoelectric point of view; it can be processed at temperatures up to 150°C, maintaining high purity and remaining electrically charged for a long time, a fact that led, together with its good biocompatibility, to its integration as biopolymer in medical applications, like drug delivery systems, artificial muscle actuators, bone and neural scaffolds etc. [19, 20, 23-25].

The electrospinning method is the best approach for obtaining long and continuous fibres, with diameters from nanometres to micrometres [7, 13, 26]. PVDF fibres can be obtained by this

* Autor corespondent/*Corresponding author*,
E-mail: cristina.busuioc@upb.ro

technique, under various conditions, such as polymer concentration, solvent type, operating details etc. [27, 28]. Fryczkowski *et al.* [29] prepared fibrous composites of PVDF and polylactide by melt electrospinning, combining the biodegradability of the first one with the chemical and mechanical benefits of the second. Damaraju *et al.* [30] obtained PVDF scaffolds containing *β*-phase by solution electrospinning, these materials being dedicated to hard tissue applications based on the ability to generate electrical activity when mechanically deformed; 20 % polymer dissolved in N,N-dimethylacetamide / acetone solvent ensured diameters between 150 and 300 nm, decreasing with voltage increase, and supported the osteogenic differentiation of human mesenchymal stem cells. He *et al.* [31] reported on electrospun drug-loaded PVDF membranes with the role of wound dressings; using N, N-dimethylacetamide / acetone for solubilization and a concentration of polymer below 15 %, fibres with diameters between 250 and 500 nm were achieved, concluding that higher concentrations generate continuous and smooth fibres and reduce the formation of beads. Kim and Kee [32] fabricated PVDF mats enhanced with bacterial cellulose nanowhiskers through electrospinning, as hybrid electro-active actuators; the mixture of N,N-dimethylformamide / acetone and 25 % polymer concentration led to a significantly improved displacement due to the synergistic effect of ion migration and electrochemical doping process when the voltage is applied. Silva *et al.* [33] synthesized ceramic/polymer biocomposites from PVDF and biphasic calcium phosphate, with applications in bone engineering; the tests revealed high bioactivity and suitable mechanical properties, that recommend them for osseous implants with postoperative recovery accelerated by external stimuli.

In this work, the electrospinning method was employed for the manufacturing of polyvinylidene fluoride fibres. Several experimental parameters related to the precursor solution or processing mode were varied with the aim of producing high-quality one-dimensional structures. In the end, the possibility of decorating them with barium titanate particles for proposing a piezoelectric composite was investigated. Such materials could be integrated into new strategies for tissue engineering, strategies that use electrical stimulating fields [34].

2.Experimental

Polyvinylidene fluoride (PVDF, $(CH_2CF_2)_n$, 275.000 g/mol), dimethylformamide (DMF, $HCON(CH_3)_2$, ≥ 99.9 %), dimethyl sulfoxide (DMSO, $(CH_3)_2SO$, ≥ 99.9 %), acetone (Ac, CH_3COCH_3, ≥ 99.9 %) and barium titanate (BT, $BaTiO_3$, 99 %, particles < 3 μm), all purchased from Sigma-Aldrich, were necessary for the experimental work.

The electrospinning technique was employed for fabricating the polymeric fibres. Thus, solutions of PVDF in single or binary solvents were prepared by magnetically stirring at 90 °C for at least 2 h. The compositional characteristics of each solution are presented in Table 1. There are three main situations when it comes to solvent: DMF, DMF+DMSO and DMF+Ac. In the last case, three different ratios were approached, as follows DMF:Ac = 1:1, 4:1, 2:3. In order to assess the effects of a solid addition in the electrospinning solution, BT commercial powder was mixed with the solvent and ultrasonicated for 10 min before the polymer was integrated into the system. For the situation of BT particles loading, the optimal experimental conditions in terms of solution characteristics and process parameters were employed.

Table 1

Composition of the electrospinning solutions / *Compoziția soluțiilor de electrofilare*

No.	Solution code	DMF *(mL)*	DMSO *(mL)*	DMF:DMSO ratio	Ac *(mL)*	DMF:Ac ratio	PVDF *(g)*
1	PVDF-DMF-**10**	10	0	-	0	-	1.0
2	PVDF-DMF-**15**						1.5
3	PVDF-DMF-**20**						2.0
4	PVDF-DMF-**DMSO**-15	5	5	**1:1**			1.5
5	PVDF-DMF-**1**-Ac-**1**-**15**	5	0	-	5	**1:1**	1.5
6	PVDF-DMF-**1**-Ac-**1**-**20**						2.0
7	PVDF-DMF-**4**-Ac-**1**-**15**	8			2	**4:1**	1.5
8	PVDF-DMF-**2**-Ac-**3**-**20**	4			6	**2:3**	2.0

Once the precursor solutions were ready (colourless, transparent, without visible inclusions), they were loaded in plastic syringes which were fixed on a syringe pump and connected to a blunt tip stainless steel needle having an inner diameter of 0.8 mm. A high voltage source was necessary to provide an electrostatic field of 15 or 18 kV. A static planar collector was placed at a distance of 15 or 20 cm from the spinneret tip, aluminium foil being attached to its surface as fibres support for subsequent samples manipulation. The feeding rate ranged between 0.2 and 1 mL/h. The electrospinning process was performed at room temperature around 22 °C and relative humidity of approximately 40 %. Finally, 3 wt% BT powder was added to the precursor solution that led to the best pristine fibres (2 g PVDF, 0.3 g BT and 10 mL solvent) and electrospun in optimal conditions.

The results were assessed with the help of a scanning electron microscopy (SEM), Quanta Inspect F electron microscope, the samples being covered with a thin layer of gold before investigation.

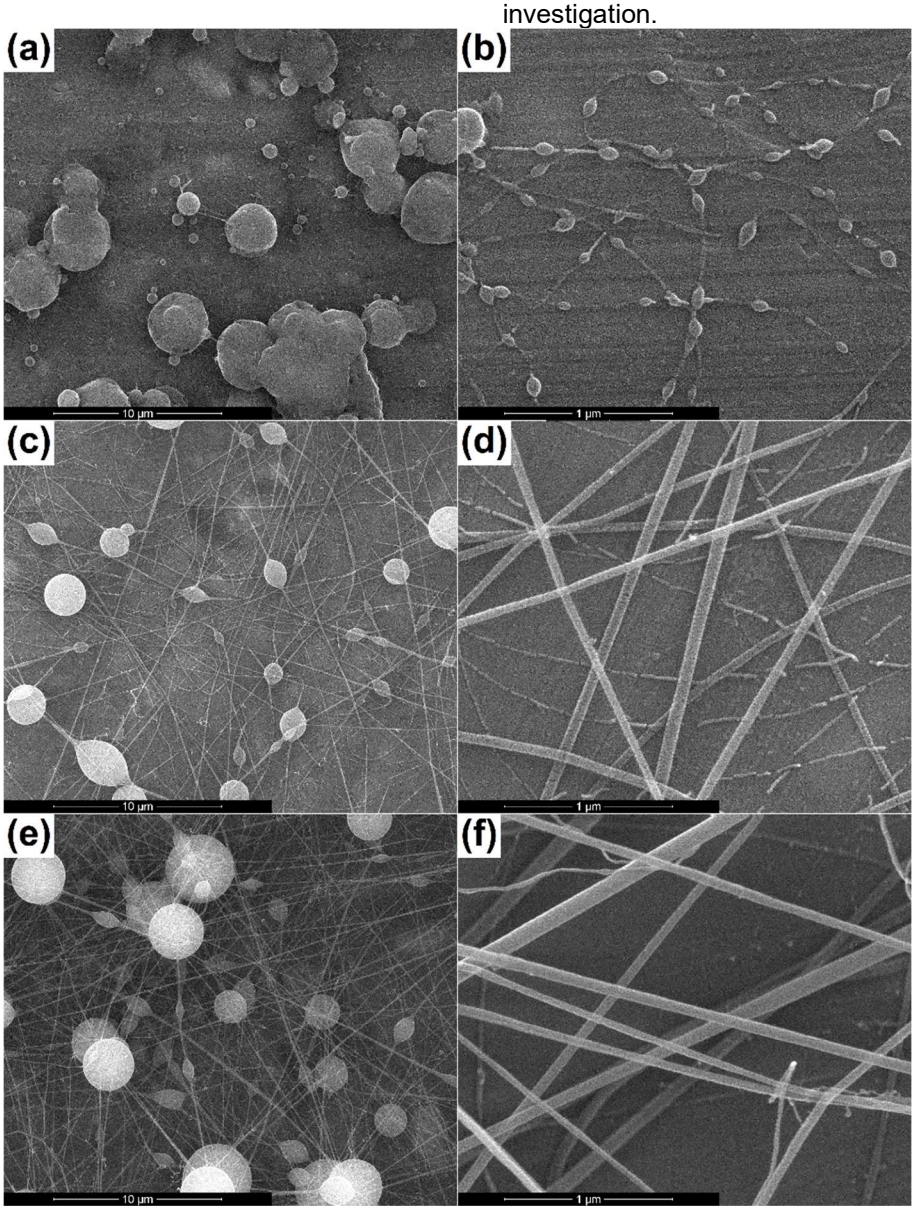

Fig. 1 - *SEM images of PVDF fibres obtained from:/ Imagini SEM ale fibrelor de PVDF obținute din:*
*PVDF-DMF-**10** solution: (a) **0.2 mL/h**, **20 cm**, 15 kV, (b) **0.5 mL/h**, **15 cm**, 15 kV;*
*PVDF-DMF-**15** solution: (c) **0.4 mL/h**, **20 cm**, 15 kV, (d) **0.7 mL/h**, **15 cm**, 15 kV;*
*PVDF-DMF-**20** solution: (e) **0.5 mL/h**, **20 cm**, 15 kV, (f) **0.7 mL/h**, **15 cm**, 15 kV.*

3.Results and discussion

The first series of samples was prepared by modifying the concentration of PVDF in DMF as a single solvent. The approached values were 10, 15 and 20 %, starting from the idea that most of the articles on this topic reported concentrations of 20 % or more [19, 35], but the dissolution process was difficult, and the viscosity of the resulting solutions seemed to be unappropriated for electrospinning at

such proportions, that is why we tried lower values. Analysing the SEM images from Fig. 1, it can be noticed that for 10 % polymer concentration, the two samples electrospun in slightly different experimental conditions were not in the form of one-dimensional structures, but as perfectly spherical entities of a few micrometres diameter (Fig. 1 a) or a continuous rough layer with protuberances and pores (Fig. 1 b). These aspects confirm that the process was mainly of electrospraying (instead of electrospinning), due to the superiority of surface tension over the electrical force; basically, the surface tension separates the jet into droplets, which constitute a much more energetically stable system.

The increase of polymer concentration to 15 % does not bring important improvements in terms of morphology: the number of spherical structures is reduced, probably because most of the material is dispersed as a uniform smooth layer over the entire substrate, while some very short and thin fibres emerge from place to place, as extensions of some spheres that occasionally become a little elongated (Figs. 1 c and d). This means that the ratio between surface tension and electrical force changes in favour of the second one, but it is still not enough for ensuring fibre stability.

The situation is quite different for the highest PVDF concentration (20 %), when a network of fine fibres occurs on the surface, together with a family of spheres (Figs. 1 e and f). They are decorated with beads, often sectioned and their diameter does not exceed 30 nm. It is well-known that polymer concentration has direct implications on the surface tension, conductivity, and viscosity of the solution. To ensure jet continuity during electrospinning, one can either use a higher molecular mass or increase the solution concentration; on the other hand, too high viscosity hinders the pumping process. Moreover, viscosity governs the formation of beads (from spherical to fusiform), such cases being reported especially for low viscosities, when the influence of surface tension is dominant. On another hand, the reduced viscosity can favour the generation of a secondary jet from the main one, which leads to fibres with different diameters or deposition on a smaller surface.

Since the use of a single solvent did not lead to well-defined fibres, we replaced DMF with a mixture of DMF and DMSO in a ratio of 1:1 and kept an intermediate concentration for the polymer (15 %). Figs. 2 a and b exhibit the results of this test, which are quite similar to the previously reported ones, namely the coexistence of quasi-spherical coarse entities and beaded frail fibres in the nanometric range. Thus, we concluded that blending DMF with a solvent having a higher boiling point (DMSO, 189 °C) is not the proper way for fibre synthesis.

Therefore, we selected a solvent with a lower boiling point (Ac, 56 °C), as the second component in the solvent mixture. By maintaining 1:1 ratio and 15 % concentration, veritable mats of fibres with diameters between 20 and 100 nm were obtained (Figs. 2 c-f). The structures are thin, but extremely long and randomly placed one above the other, as multi-layered non-woven webs. The formation along the fibre length of spherical or ellipsoidal formations with a diameter larger than the diameter of the host fibre (beads-on-string) is also related to the surface tension of the precursor solution; the electrical charges acting on the jet must be high enough to exceed the value of its surface tension. The changes in feeding rate and spinneret-collector distance led to visible differences in fibre density (to be expected considering that more material is pumped), as well as beads number and shape (to be explained based on the travelling time towards the collector; a higher distance is equal to a longer time for fibre thinning and beads elongation/elimination).

The next step was to increase PVDF concentration to 20 % to generate thicker fibres that could be appropriate for the development of tissue engineering devices. Fig. 3 shows the SEM images of such fibres synthesized by varying the flow and voltage. The samples are similar, with fibres having a disorderly arrangement, a large diameter distribution (from 100 to 800 nm) and a homogeneous spreading of the constitutive beads. This time, the beads are more elongated, and they do not affect the integrity and continuity of the fibres. On the contrary, these areas of diameter enlargement could act as favourable zones when it comes to the electrical properties (piezoelectric effect), with subsequent implications on the possibility of creating a stimulating field for controlled tissue regeneration.

Another direction was built on the idea of testing the influence of the solvents ratio on the aspect of PVDF fibres. A DMF:Ac ratio modified in favour of DMF (DMF:Ac = 4:1) triggered the morphologies presented in Fig. 4. Compared to Figs. 2 c-f, where the polymer concentration is identical (15 %), it can be observed that a major content of DMF is detrimental for fibres formation: there are fibres only on reduced areas, they are thin, breakable and sometimes composed of a succession of beads. The spherical or quasi-spherical structures are both big and independent, as well as small and integrated into fibres. Analysing comparatively, it is obvious that the prevalence of a solvent with a high boiling point (DMF, 153 °C) is not beneficial for the electrospinning process. The solvent evaporation rate is closely correlated with the precursor solution viscosity when traveling from spinneret to collector. If the evaporation rate is low, the solution viscosity is maintained at a high level for a longer period, which favours the thinning process in the electric

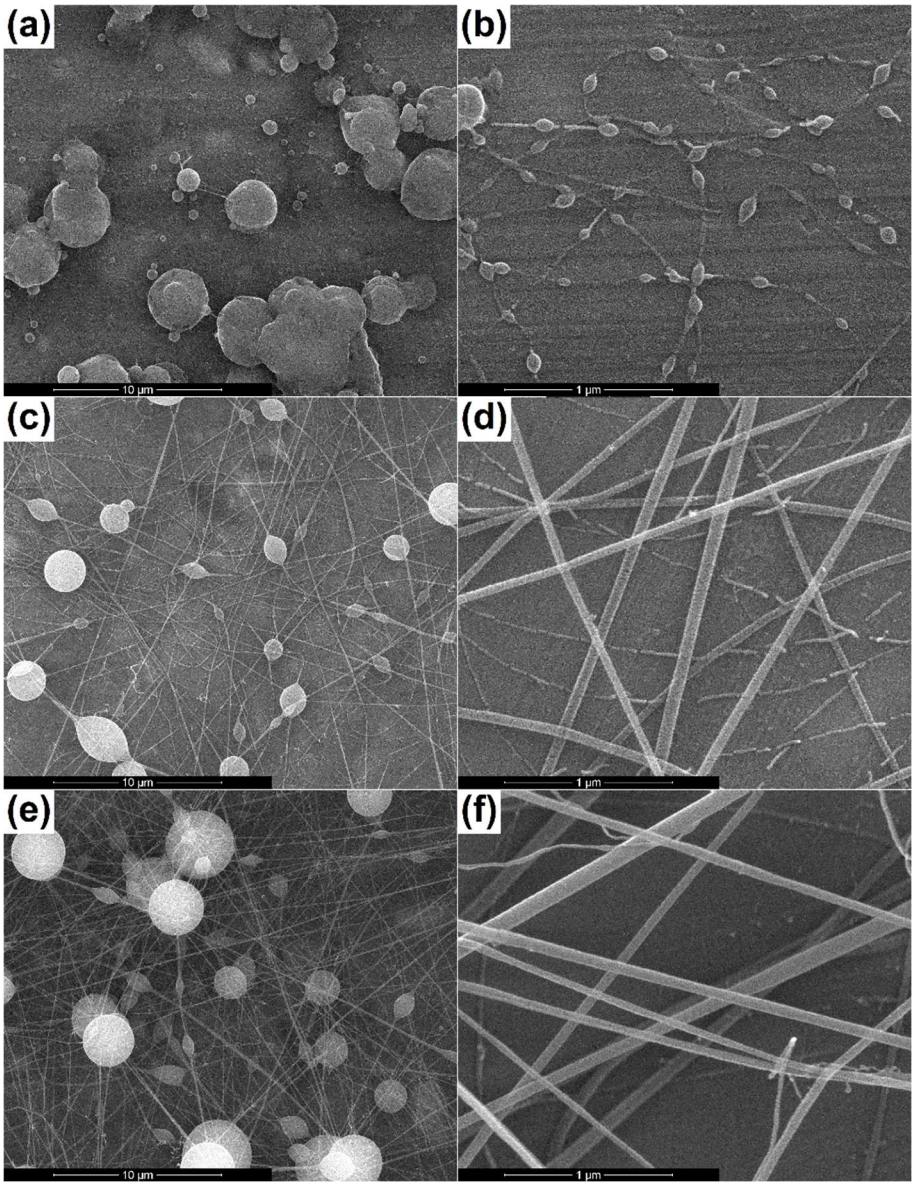

Fig. 2 **-** SEM images of PVDF fibres obtained from:/ *Imagini SEM ale fibrelor de PVDF obținute din:*
*(a and b) PVDF-DMF-**DMSO**-15 solution (0.2 mL/h, 20 cm, 15 kV);*
*PVDF-DMF-**1**-Ac-**1**-**15** solution: (c and d) **0.5 mL/h**, **20 cm**, 15 kV;*
*(e and f) **0.7 mL/h**, **15 cm**, 15 kV.*

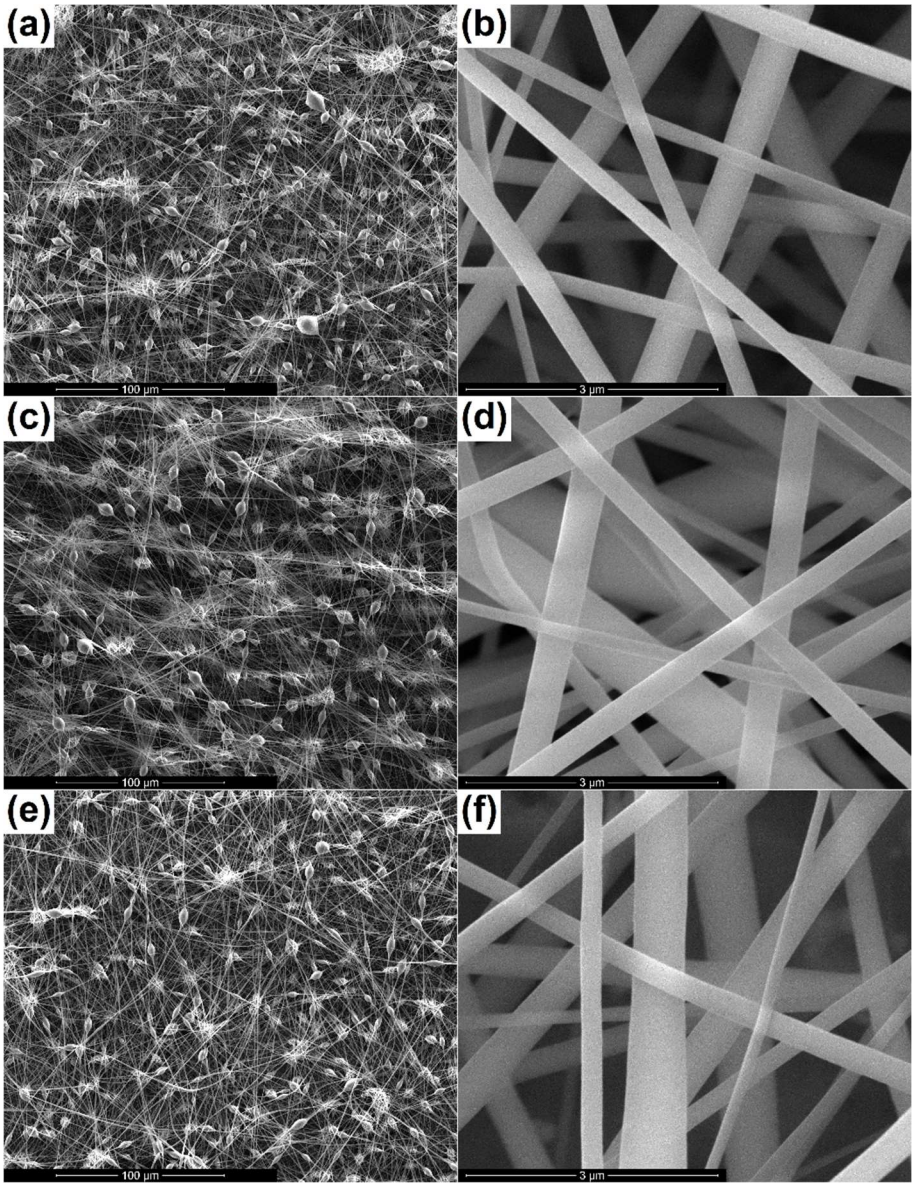

Fig. 3 - SEM images of PVDF fibres obtained from PVDF-DMF-**1**-Ac-**1**-**20** solution:
*Imagini SEM ale fibrelor de PVDF obținute din soluție de PVDF-DMF-**1**-Ac-**1**-**20**:*

*(a and b) **0.5 mL/h**, 20 cm, **15 kV**;*
*(c and d) **1.0 mL/h**, 20 cm, **15 kV**;*
*(e and f) **1.0 mL/h**, 20 cm, **18 kV**.*

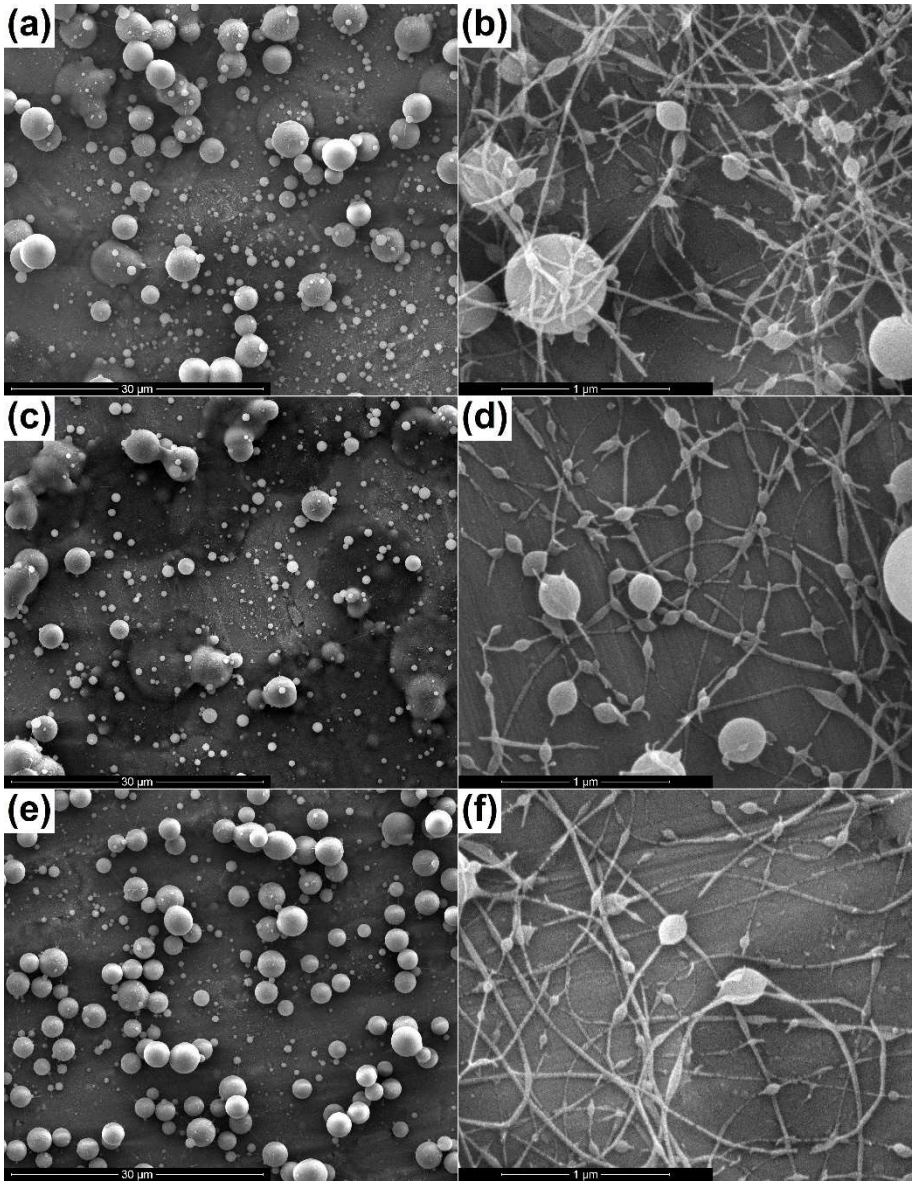

Fig. 4 - SEM images of PVDF fibres obtained from PVDF-DMF-**4**-Ac-**1**-**15** solution:
*Imagini SEM ale fibrelor de PVDF obținute din soluție de PVDF-DMF-**4**-Ac-**1**-**15**:*
*(a and b) **0.5 mL/h**, 20 cm, **15 kV**;*
*(c and d) **1.0 mL/h**, 20 cm, **15 kV**;*
*(e and f) **1.0 mL/h**, 20 cm, **18 kV**.*

field and ultimately leads to the deposition of thinner fibres; at the other extreme, if the evaporation rate is high, the solution viscosity increases suddenly after the jet leaves the spinneret tip, fact that hinders the process of fibres thinning, sometimes even making it impossible to obtain the primary jet. In our case, DMF evaporation rate is so slow, that the solution viscosity remains low for a longer stage and the jet becomes unstable under the high voltage, allowing its disintegration into droplets under the action of surface tension.

The best situation was achieved when modifying the solvents ratio in favour of Ac, namely a DMF:Ac ration of 2:3, and increasing the polymer concentration up to 20 %. The SEM images displayed in Fig. 5 validate this statement through the homogeneous aspect of the mats, low proportion of beads, good quality of the fibres and average diameter of 600 nm (Figs. 5 b, d and f). Indeed, there are some fusiform entities from place to place, but their diameter is not so increased compared to the host fibre. It seems that the increase of the feeding rate contributes to the emergence of more beads (Fig. 5 a *vs.* Fig. 5 c) due to the pumping of a larger amount of material, while the spinneret-collector distance is kept constant (20 cm) and the polymeric jet is thinned to a lower extent. On the contrary, the increase of the applied voltage removed most of the beads (Fig. 5 c *vs.* Fig. 5 e) because it generates more charge carriers in the solution, which in turn will affect jet velocity and fibre stretching, with implications for the

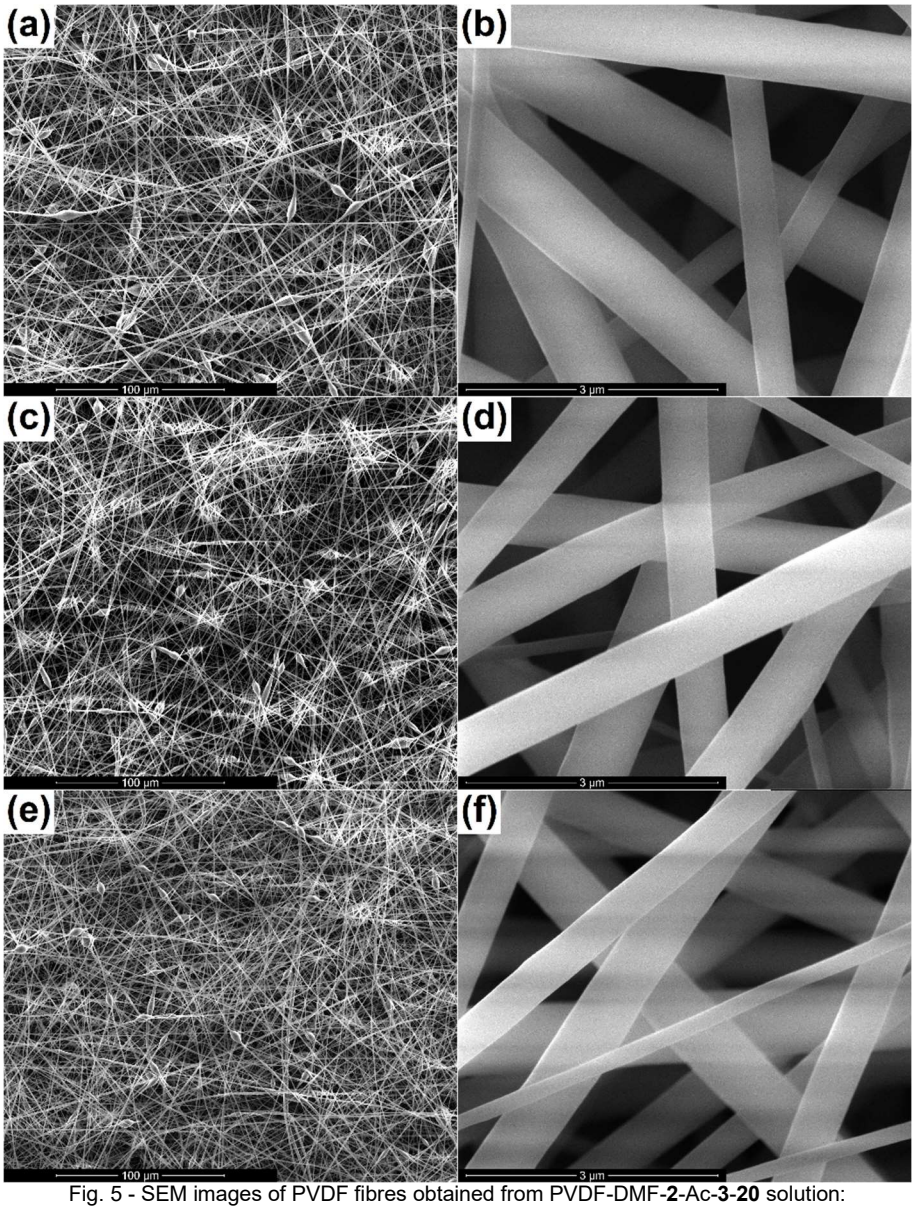

Fig. 5 - SEM images of PVDF fibres obtained from PVDF-DMF-**2**-Ac-**3**-**20** solution:
*Imagini SEM ale fibrelor de PVDF obținute din soluție de PVDF-DMF-**2**-Ac-**3**-**20**:*
*(a and b) **0.5 mL/h**, 20 cm, **15 kV**;*
*(c and d) **1.0 mL/h**, 20 cm, **15 kV**;*
*(e and f) **1.0 mL/h**, 20 cm, **18 kV**.*

evaporation rate of the solvent, respectively the final diameter of the fibres; thus, a higher applied voltage leads to thinner and drier fibres.

In conclusion, the following operating conditions were established as optimal: DMF:Ac ratio of 2:3, PVDF concentration of 20 %, 1.0 mL/h feeding rate, 20 cm distance, 18 kV applied voltage.

As a last experiment, we added BT commercial powder (a well-known ceramic with piezoelectric properties) in a proportion of 3 wt% in the precursor solution to study the possibility of producing composite materials based on a polymeric phase and an inorganic one, as a starting point for the fabrication of multifunctional materials dedicated to tissue engineering. The morphology of the employed powder is available in Figs. 6 a and b; it contains polyhedral particles with round edges and corners, not exceeding 1 µm in size and most of the time gathered in bunches. The presence of such aggregates in the electrospinning solution did not cause a major disturbance for the process. As general remarks, a little denser web is available, the diameter of the fibres is slightly higher (700 nm average diameter) and the beads content is almost removed. The particles are encapsulated in the fibres volume, without affecting their long-range continuity or increasing their diameter too much. To assess BT distribution, SEM images obtained in the secondary electron mode (Figs. 6 c and d) are accompanied by their counterparts obtained in the back-scattered electron mode (Figs. 6 e and f). The inorganic powder is spread homogeneously on a large area, the difference in composition between polymer and ceramic being highlighted through the lighter and darker zones.

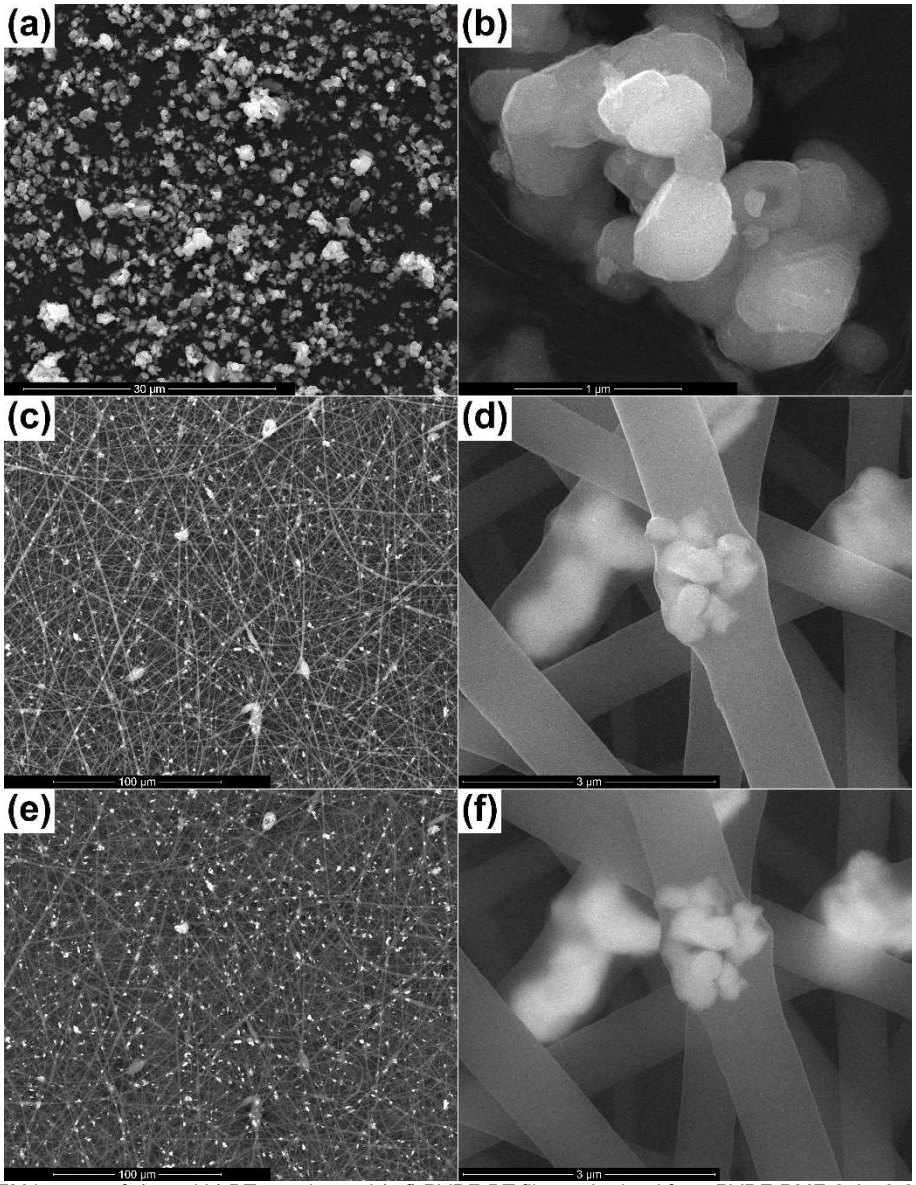

Fig. 6 **-** SEM images of: (a and b) BT powder and (c-f) PVDF-BT fibres obtained from PVDF-DMF-**2**-Ac-**3**-**20** solution with **3 wt% BT** powder (1.0 mL/h, 20 cm, 18 kV). Images (c and d) are obtained using secondary electrons, while images (e and f) are obtained using back-scattered electrons.
*Imagini SEM ale: (a și b) pulberii de BT și (c-f) fibrelor de PVDF-BT obținute din soluție de PVDF-DMF-**2**-Ac-**3**-**20** cu **3 %grav BT** pulbere de (1,0 mL/h, 20 cm, 18 kV). Imaginile (c și d) sunt obținute utilizând electroni secundari, în timp ce imaginile (e și f) sunt obținute utilizând electroni retro-împrăștiați.*

4.Conclusions

Polyvinylidene fluoride fibres with smooth surface, long-range continuity and a low proportion of beads were synthesized by the electrospinning method. The influence of solvent type, polymer concentration and operating parameters was investigated, and the following parameters were established as optimal: a ratio of 2:3 between dimethylformamide and acetone, a concentration of 20 % polyvinylidene fluoride, a feeding rate of 1 mL/h, a distance between spinneret and collector of 20 cm and an applied voltage of 18 kV. The obtained webs were homogeneous, multi-layered, and composed of randomly distributed fibres with an average diameter of 600 nm. The addition of 3 wt% barium titanate powder as inorganic decoration did not change the general features of the fibrous material, but demonstrated the possibility of fabricating a piezoelectric composite with potential synergistic behaviour. Such scaffolds can be further expanded to propose new and improved materials for the field of tissue engineering.

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