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THE EFFECT OF FLOW RATE AND NEEDLE DIAMETER ON THE FORMATION OF POLY(ETHYLENE-TEREPHTHALATE) NANOFIBER

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Abstract
Poly(ethylene-terphthalate) (PET) was electorspun using constant PET concentrations (15 wt %) in Trifluoroacetic acid (TFA) and Dichlormethae (DCM) solution (50:50 ratio of solvents). The applied voltage and the distance between the needle and the ground collector kept constant, while the flow rate of polymer solution was varied from 0.005 to 0.05 ml/min and two needle diameters were used. The effect of solution flow rate and needle diameters on the fiber formation was investigated for better control of the electrospinning process. The resulting nanofibers were observed using Scanning Electron Microscopy (SEM). The obtained results showed nanofibers formation with droplets and beads formation, however, at critical flow rates of PET solution uniform beadless electrospun nanofibers was organized, and uniform morphology of nanofiber was obtained.

Keywords: Electrospinning, PET, Flow Rate, SEM, Nanofiber.

الملخص
تم غزل البولي إيثيلين تيرفثاليت (PET) بواسطة جهاز الغزل إلكترونية و باستخدام تركيز ثابتة من البوليمير (15% نسبة وزنية) في محلول من دايكلوروميثان (DCM) و حمض ثيترافلورواستيك (TFA) و نسبة 50:50 من المذيبات. ظل الجهد المطبق والمسافة بين الإبرة والمجمع الأرضي ثابتًا، بينما كان معدل تدفق محلول البوليمر يتراوح من 0.005 إلى 0.05 مل/دقيقة كما تم استخدام قطرين مختلفين من الإبرة

.وقد تم فحص تأثير معدل تدفق المحلول وأقطار الإبرة على تكوين الألياف من أجل تحكم أفضل في عملية الغزل الكهربائي .تمت ملاحظة تكون الألياف النانوية الناتجة وذلك باستخدام الفحص المجهري الإلكتروني(SEM). وقد أظهرت النتائج التي تم الحصول عليها تكوين ألياف نانوية مع تكوين قطرات وحبيبات ، ومع ذلك ، لمحلول PETوعند معدلات التدفق الحرجة تم الحصول على ألياف نانوية متجانسة و بدون خرزة من خلال جهاز الغزل إلكترونية ، وتم الحصول على شكل مرفولوجي موحد لهذه للألياف النانوية.

1. Introduction

Nowadays electrospinning has become the most widely used technique in producing nanofibers material [1]. Since its first use in the early 20th century, significant improvements have been made in the instrument design, material used, and nanomaterials produced [2]. Fibers produced by electrospinning approach are smaller in diameter than those produced by conventional fiber production methods like melt or solution spinning [3]. The average diameter of these submicron polymeric fibers are in the range of 10 nm to 1 μm [4-6]. Examples of application of nanofibers are in tissue engineering, drug delivery systems, wound dressings, antibacterial study, filtration, desalination, protective clothing fabrication, and biosensors. Several reviews have comprehensively summarized significant advances in the electrospinning area [7,8].

An electrospinning apparatus includes a pump, a needle, a high voltage power supply, and a collector [9]. During electrospinning, a precursor solution is pumped and forced through a narrow orifice to form dependent droplets at the needle tip. As the voltage increases, the repulsive force pulls out the solution into a Taylor cone. Once the voltage reaches a critical value, the repulsive force overcomes the surface tension of the solution and a liquid jet is ejected from the Taylor cone to the collector. During this process, the fiber jet experiences whipping and bending to allow the solvent to evaporate before fibers are accumulated on the collector, and the whole process usually takes place in milliseconds [9,10].

Electrospinning technique offers an attractive method for mimicking the natural extracellular matrix for tissue engineering applications. However, a major problem in electrospinning is the accumulation of fibres and beads formations, which can be limited by controlling several parameters. The production of nanomaterials (nanofibers) via electrospinning is affected by many operating parameters such as applied electric field, distance between the needle and collector and flow rate, needle diameter. However, other parameters have great affect on the nanofibers fabrication such as solution parameters (polymer concentration, viscosity, solvent and solution conductivity) and environmental parameters (relativity humidity and temperature). These different parameters can also be used to control the fabrication of fibers [11,12].

The flow rate of the polymer solution may determine the morphology of the produced nanofibers. Uniform bead free electrospun nanofibers might be prepared via a critical flow rate. The value of the critical flow rate varies with the polymer types. In some cases increasing the flow rate above the critical value lead to the formation of beads, as reported for polystyrene, when the flow rate was increased to 0.10 mL/min, bead formation was observed. However, when the flow rate was reduced to 0.07 mL/min, bead-free nanofibers were formed. Increasing the flow rate beyond a critical value not only leads to increase in the fibre diameter but also to bead formation (due to incomplete drying of the nanofiber jet during the flight between the needle tip and metallic collector) [13]. Because increases and decreases in the flow rate affect the nanofiber formation and diameter, a minimum flow rate is preferred to maintain a balance between the leaving polymeric solution and replacement of that solution with a new one during jet formation[14]. In addition to bead formation, at high flow rate, ribbon-like defects and droplets have also been reported in the literature [13,15].

Furthermore few studies contributed to investigate the effect of needle diameter on the electrospun nanofiber production and diameter. One study by Macossay el al. reported that there is no correlation between the needle diameter and electrospun poly methyl methacrylate (PMMA) nanofibers [16]. While other studies

show very clear effect to the needle diameter, when different polymer systems were used [17,18].

On the light of the previous mentioned complexity of the electrospinning process parameters, only two operating parameters are chosen to be investigated in this paper, namely the flow rate and the needle diameter. Poly(ethylene-terphthalate) (PET) was used in this study. Poly(ethylene-terphthalate) is a semi crystalline polymer and a thermo plastic, made by melt polymerization, which is heavily used in engineering. It is soluble in few solvents, the most effective solvents being Trifluoroacetic acid (TFA) and O-ChloroPhenol (OCP) [19,20]. PET is used in a variety of applications due to its resistant to environmental effects and good mechanical properties [21]. It is used in the automotive and packaging industry extensively, however lately PET nanofiber mats were used for filtration [22], protective clothing [23], and tissue engineering scaffolds [24].

In this research a constant PET concentration in mixture of Trifluoroacetic acid (TFA) and Dichlormethae (DCM) solution are used. The applied voltage and the distance between the needle and the ground collector are also kept constant. The flow rate of polymer solution was varied from 0.005 to 0.05 ml/min and two needle diameters were used.

2. Experimental Work

High purity Poly(ethylene-terphthalate) with 40,000 molecular mass (Mn) was obtained from Polymer Analytic Lab., and was used in this study as received. The complete characterization of this polymer is shown in Table 1. Poly(ethylene-terphthalate) solution was prepared in mixture of TFA and DCM, and the obtained solutions was continuously stirred for sufficient time (from 2 to 3 hours) at room temperature to increase homogeneity.

TABLE 1. Poly(ethylene-terphthalate) Characteristics and Properties.

M_n (g/mol)	M_w (g/mol)	Polydispersity	Melting temperature (k)	Glass temperature (k)
40,000	62,000	1.52	525	350

Figure (1) illustrates the applied electrospinning apparatus, in its simplest form. The experimental set-up consisted of a 10-ml syringe to hold the polymer solution and stainless steel needle, a syringe pump, two electrodes, a DC voltage supply in the kV range, and a ground collector (see Figure (1)). The variable high voltage supply (built in-house and capable of a voltage up to 50 kV) was used to apply a potential difference between the spinneret and the grounded collector plate. The presence of polymer in solution leads to the formation of fine solid fibres as the solvent evaporates. The charge on the fibres eventually dissipates into the surrounding environment [25]. A Hamilton SGE gas tight syringe used as the spinning solution reservoir was placed in a Kent Scientific (model: Genie Plus) pump, which fed the PET solution through a needle (gauge 26) at specified predetermined rate.

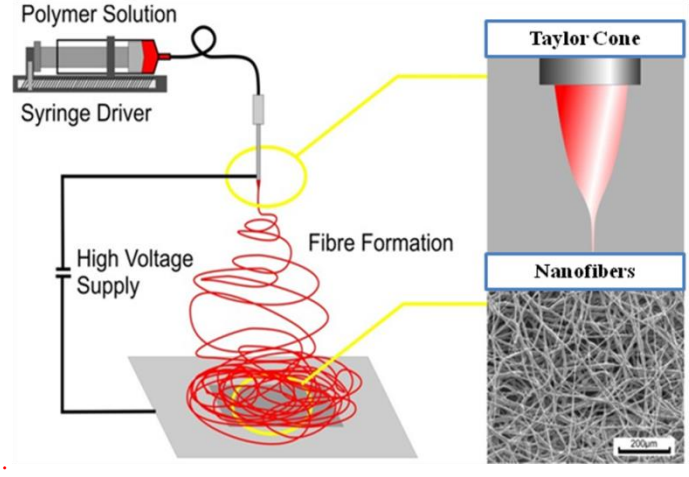


Figure 1. Schematic representation of the applied electrospinning process.

In order to investigated the effect of polymer solution flow rate on the nanofibre diameter and formation four different volumetric flow rate are used namely 0.05, 0.02, 0.01 and 0.005 ml/min. (15% wt.) poly(ethylene-terphthalate) concentrations was used in mixture of solvents (TFA and DCM) with 50:50 volume percent. In all the experiments a voltage of 15 kV was kept constant and

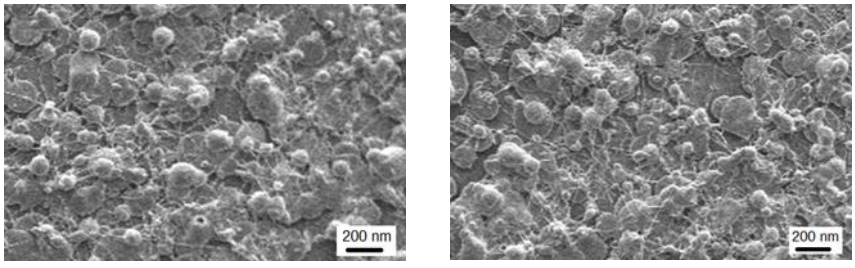
was applied to the solution and the solution jet emerging from the needle was collected on the aluminum foil ground collector. The distance between needle tip and collector was also constant at 15 cm, room temperature and relative humidity were 25 ºC and 65%, respectively. To consider the effect of the needle diameter in the electrospinning process two size of needle diameters were used 0.26 and 0.21 mm.

Scanning Electron Microscope (SEM) analysis was done to confirm the nanofibers formation and to obtain the morphology of the electrospun nanofibres. The instrument used was a Zeiss Merlin Field Emission Scanning Electron Microscope (FE-SEM) with the Zeiss Smart-SEM software. The electrospun nanofibre mats were loaded into the chamber of the SEM instrument and images were recorded under vacuum at 7 kV voltage with 250 pA beam current and a working distance of 4.0 mm, the column was in high resolution mode.

3. Results and Discussion

SEM micrographs of Poly(ethylene-terphthalate) (PET) nanofibers obtained using four different flow rates and with two different types of needle diameters are presented in Figures from Figure (2) to Figure (5).

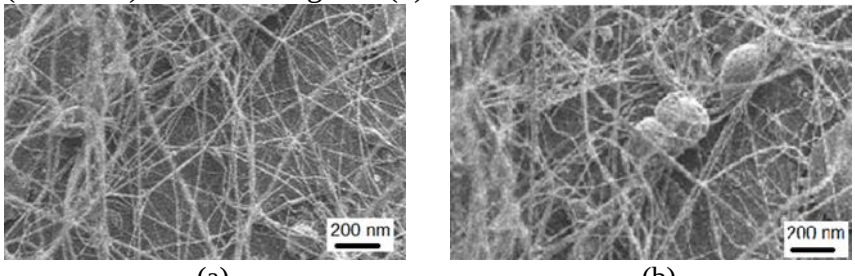
Figure 2(a) and 2(b) present the SEM for nanofibers fabricated using 0.05 ml/min flow rate using needles with 0.26 mm and 0.21 mm internal diameter (ID), respectively. In this figure one can see very small length nanofibers formed in-between the large droplets or agglomeration of polymer that clearly observed in SEM image. The agglomeration of PET formation can be due to the chain entanglement and aggregate because the insufficient solvent evaporation. Small changes in the electrospun fibres (determined using SEM micrographs) were obtained by varying the needle diameter from 0.21(Figure 2(a)) to 0,26 mm (Figure 2(b)).



(a) (b)

Figure 2. SEM micrographs of PET nanofibers using 0.05 ml/min, flow rate and (a) 0.21 mm (b) 0.26 mm ID of needle

As shown in Figures 3 (a) and 3(b), PET electronspun using 0.02 ml/min, flow rate produced nanofibers that are beaded and branched in shape with a few of agglomeration. The agglomeration are seen more frequently in the case of larger needle diameter (0.26 mm) as seen in Figure 3(b).

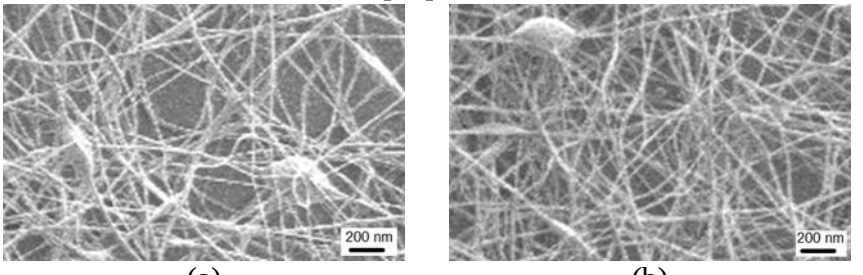


(a) (b)

Figure 3. SEM micrographs of PET nanofibers using 0.02 ml/min, flow rate and (a) 0.21 mm (b) 0.26 mm ID of needle.

In addition to that, the average diameter for 25 individual nanofibers of each sample was measured. The results show that large needle diameter (0.26 mm), give nanofibers with average diameter of 107 nm ± 32, while smaller needle diameter (0.21 mm), give nanofibers with average diameter of 93 nm ± 40. This difference in the nanofiber diameters might be explained as following; when small needle diameter is used a small drop will

form from the polymer solution at the tip of the needle, while in the case of using large needle diameter large drop will form. The small drop will has high surface tension compared with the large one needle, which needs very high potential difference to overcome the surface tension and form polymer jet. The high potential difference increases a force called electrostatic force which is responsible about stretching the polymer jet, so thinner nanofibers will be formed and collected on the ground plate, in the case of small needle diameter [17].

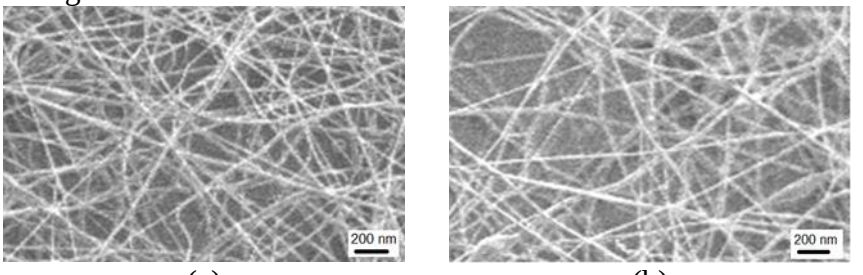


(a) (b)

Figure 4. SEM micrographs of PET nanofibers using 0.01 ml/min, flow rate and (a) 0.21 mm (b) 0.26 mm ID of needle.

Figures 4(a) and 4(b) present the SEM for nanofibers fabricated using 0.01 ml/min flow rate using needles with different needle diameter. As shown in Figures (3) in both Figures 4(a) and 4(b), PET nanofibers is produced with less beads and agglomeration. However, ribbon-like structure is obtained in several images as seen two of them in Figure 4(a) and one in Figure 4(b). The formation of beads and ribbon-like structures could be mainly attributed to the large amount of solvent that needed to be evaporated as well as to the low stretching of the solution in the flight between the needle and metallic collector. The presence of such beads and ribbon-like structures could be also attributed o the influence of the gravitational force [15]. The same effect could also be attributed to an increase in diameter of the nanofibers with an increase in the flow rate [26]. The average diameter for the large needle diameter (0.26 mm), the average diameter was 102

nm ± 25, while for the smaller needle diameter (0.21 mm), the average diameter was 88 nm ± 43.



(a) (b)

Figure 5. SEM micrographs of PET nanofibers using 0.005 ml/min, flow rate and (a) 0.21 mm (b) 0.26 mm ID of needle

Figures 5 (a) and 5(b), demonstrate the electrospun nanofibers obtained using 0.005 ml/min, flow rate by 0.21, 0.26 mm needle diameters. In this case thinner, smoother and bead free without agglomeration nanofibers was observed with both small and large needle diameter compared with nanofibers previously obtained by large PET solution flow rates. The average nanofibers diameter in the case of 0.26 mm needle diameter was 95 nm ± 27, while with 0.21 mm, the average diameter was 82 nm ± 38.
Therefore, with small needle diameter, the nanofibers were thinner.

The nanofibers average diameter variations as a result of PET solution flow rate change and due to using two different sizes (diameters) of needle are shown in Figure (6).

In general there is clear trend with positive proportion as the flow rate increases the average diameters increased and as the needle diameter increases the average diameters increased as well. Furthermore, the large variation in the nanofibers diameters distribution as shown from the standard deviation values for smaller needle diameter when compared with large needle diameter. This could be due to cone jets formation secondary stable and not stable jet cone formation during the electrospinning process, these jets are continuously replaced by cone jets. As a

result of this phenomenon, nanofibers with a wide range diameter are formed [15].

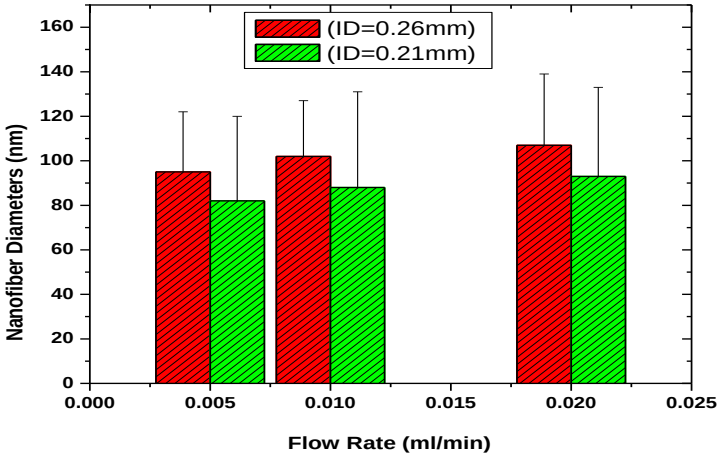


Figure 6. The nanofibers average diameter change with PET solution flow rate change and using different needle diameters.

From the resulting images, in general, it is observed that the increasing of Poly(ethylene-terphthalate) solution flow rate leads to increase the diameter of nanofibers. This can be due to the increasing in the chain entanglement as the solvent evaporated. On the other hand, the lower the flow rate the more solvent will evaporated and stable nanofibers will form, and this appeared to lead to decrease the diameter of the nanofibers, as the polymer cone will stretch much longer after the solvent has been evaporated. On the other hand, when the Poly(ethylene-terphthalate) solution flow rate is very high, the polymer chains may not have enough to construct stable nanofibers due to the large quantity of solvent that needed to be evaporated.

4. Conclusions

Electrospinning is a rapid, simple, and relatively inexpensive method to fabricate high aspect ratio, submicron diameter size fibres with high surface area. In this paper, the effect of flow rate

and needle diameter on the morphology of electrospun PET nanofibers was investigated. It was found that:

1) Decreasing the PET solution flow rate from 0.05 to 0.005 ml/min, lead to decreasing in the nanofiber diameter and less bead formation was observed, which may leads to decreasing the pore.

2) Small needle diameters with 0.21 mm ID produced thinner and often beadless nanofibres (fibres without agglomeration) compared with large needle diameter 0.26 mm. These results contributed to electrostatic force, which responsible about stretching and thinning the polymer jet.

References

[1]. Reneker, D.H., Yarin, A.L., Electrospinning jets and polymer nanofibers. Polymer (2008), 49 (10), 2387–2425.

[2]. Adnan Haider , Sajjad Haider, Inn-Kyu Kang, A comprehensive review on the effect of electrospinning parameters and potential applications of nanofibers in biomedical technology, Arabian Journal of Chemistry (2018), 11, 1165–1188.

[3]. Srinivasan, G.; Reneker, D. H. Structure and Morphology of Small Diameter Electrospun Aramid Fibres, Polymer International (1995), 36, 195-201.

[4]. Doshi, J.; Reneker, D. H. Electrospinning Process and Applications of Electrospun Fibers. Journal of Electrostatics, Journal of Electrostatics (1995), 35, 151-160.

[5]. Deitzel, J. M.; Kleinmeyer, J. D.; Hirvonen, J. K.; Beck Tan, N. C. Controlled Deposition and Collection of Electro-spun Poly(ethylene oxide) Fibers Polymer (2001), 42, 8163-8170.

[6]. Deitzel, M., Kleinmeyer J., Harris D., and Beck Tan N., The Effect of Processing Parameters on the Morphology of Electrospun Nanofibers and Textiles, Polymer (2001), 1(42), 261-272.

[7]. Ramakrishna, S.; Fujihara, K.; Teo, W.-E.; Lim, T.-C.; Ma, Z., An Introduction to Electrospinning and Nanofibers. (2005), First ed.; World Scientific Publishing Company, Singapore.

[8]. Thandavamoorthy, S.; Bhat, S.; Tock, R. W.; Parameswaran, S.; Ramkumar, S. S., Electrospinning of nanofibers, Journal of Applied Polymer Science (2005), 96(2), 557-569.

[9]. Rieger, K. A.; Birch, N. P.; Schiffman, J. D. Designing Electrospun Nanofiber Mats to Promote Wound Healing-a Review. J. Mater. Chem. B (2013), 1 (36), 4531–4541.

[10]. Montinaro, M.; Fasano, V.; Moffa, M.; Camposeo, A.; Persano, L.; Lauricella, M.; Succi, S.; Pisignano, D. Sub-Ms Dynamics of the Instability Onset of Electrospinning. Soft Matter (2015), 11 (17), 3424–3431.

[11]. Zong, X.; Kim, K.; Fang, D.; Ran, S.; Hsiao, B. S.; Chu, B. Structure and Process Relationship of Electrospun., Bioabsorbable Nanofiber Membranes (2002), 43, 4403–4412.

[12]. Thompson, C. J.; Chase, G. G.; Yarin, A. L.; Reneker, D. H. Effects of Parameters on Nanofiber Diameter Determined from Electrospinning Model. Polymer. (2007), 48 (23), 6913–6922.

[13]. Megelski, S., Stephens, J.S., Bruce Chase, D., Rabolt, J.F., Micro- and nanostructured surface morphology on electrospun polymer fibers. Macromolecules (2002). 35 (22), 8456–8466.

[14]. Zeleny, J., The role of surface instability in electrical discharges from drops of alcohol and water in air at atmospheric pressure. J. Franklin Inst (1935), 219 (6), 659–675.

[15]. Shamim, Z., Saeed, B., Amir, T., Abo Saied, R., Rogheih, D., The effect of flow rate on morphology and deposition area of electrospun nylon 6 nanofiber. J. Fabrics Fibers, (2004) 4, 42-47.

[16]. Macossay, J., Marruffo, A., Rincon, R., Eubanks, T., Kuang, A., Effect of needle diameter on nanofiber diameter and thermal properties of electrospun poly (methyl methacrylate). Polymers for Advanced Technologies (2007), 18(3), 180-183.

[17]. Supaphol, P., and Chuangchote, S., On the electrospinning of poly (vinyl alcohol) nanofiber mats: a revisit. Journal of Applied Polymer Science (2008), 108(2), 969-978.

[18]. Bassam M. Abunahel, Nurul Z., Noor A., Munirah J., Effect of Needle Diameter on the Morphological Structure of Electrospun n-Bi2O3/Epoxy-PVA Nanofiber Mats International Scholarly and Scientific Research & Innovation (2018), 12(6) 296- 299.

[19]. Edgar O.B. and Hill R., The p-phenylene linkage in linear high polymers: Some structure–property relationships, J. Polym. Sci., (1952), 8,1-12.

[20]. Fakirov S., Fischer E.W., and Schmidt G.H., Unit cell dimensions of poly (ethylene terephthalate), Makromol. Chem., (1975), 176, 2459-2466.

[21]. Rajabinezhad H, Mansouri N, Yazdanshenas ME., Recycling of used bottle grade polyethylene terephthalate to nanofibers by melt-electrospinning method. International Journal of Environmental Research (2009), 3(4): 663-670.

[22]. Strain IN, Wu Q, Pourrahimi AM, Hedenqvist MS, Olsson RT, Electrospinning of recycled PET to generate tough mesomorphic fibre membranes for smoke filtration. J Mater Chem (2015), A 3: 1632-1640.

[23]. Baji A., Agarwal K., Oopath SV., Emerging Developments in the Use of Electrospun Fibers and Membranes for Protective Clothing Applications. Polymers (Basel) (2020), 12: 492-498.

[24]. Ma Z., Kotaki M., Yong T., He W., Ramakrishna S., Surface engineering of electrospun polyethylene terephthalate (PET) nanofibers towards development of a new material for blood vessel engineering. Biomaterials (2005), 26: 2527-2536.

[25]. Patanaik, A.; Anandjiwala, R. D.; Rengasamy, R. S.; Ghosh, A.; Pal, H., Nanotechnology in fibrous materials–a new perspective, Textile Progress (2007), 39(2), 67-120.

[26]. Li, Z., Wang, C., Effects of Working Parameters on Electrospinning. One-Dimensional Nanostructures. Springer, Berlin, Heidelberg (2013), pp. 15–28.