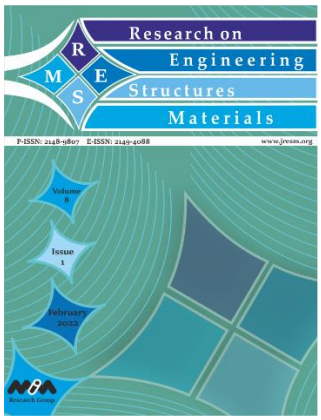
Research on Engineering Structures & Materials
journal homepage: http://www.jresm.org
Research Group



Synthesis and air permeability of electrospun PAN/PVDF nanofibrous membranes

Atike Ince Yardimci, Mehmet Kayhan, Aslı Durmus, Mehmet Aksoy, Ozgur Tarhan

Online Publication Date: 05 Jan 2022
URL: http://www.jresm.org/archive/resm2022.357na1027.html
DOI: http://dx.doi.org/10.17515/resm2022.357na1027

Journal Abbreviation: *Res. Eng. Struct. Mater.*

To cite this article
Yardimci AI, Kayhan M, Durmus A, Aksoy M, Tarhan O. Synthesis and air permeability of electrospun PAN/PVDF nanofibrous membranes. *Res. Eng. Struct. Mater.*, 2022; 8(2): 223-231.

Research on Engineering Structures & Materials
journal homepage: http://www.jresm.org
MIM Research Group

Research Article

Synthesis and air permeability of electrospun PAN/PVDF nanofibrous membranes

Atike Ince Yardimci[*1,a], Mehmet Kayhan[2,b], Aslı Durmus[3,c], Mehmet Aksoy[2,d], Ozgur Tarhan[4,e]

[1] *Usak University, Technology Transfer Office, Usak, Turkey*
[2] *Usak University, Scientific Analysis, Technological Application and Research Center, Usak, Turkey*
[3] *Usak University, Department of Molecular Biology and Genetics, Usak, Turkey*
[4] *Usak University, Department of Food Engineering, Usak, Turkey*

Article Info

Article history:
Received 27 Oct 2021
Revised 02 Jan 2022
Accepted 03 Jan 2022

Keywords:

Polyacrilonitrile/Polyvinylidene fluoride;
Nanofiber;
Electrospinning;
Membrane;
Air filter

Abstract

Electrospun nanofibers present well-design membranes for filtration applications. In this study, the synthesis of polyacrylonitrile (PAN)/polyvinylidene fluoride (PVDF) bicomponent nanofibers was reported for air filtration application. Polymer concentration effect on the morphology of PAN/PVDF nanofibers was investigated and 10, 20, 30, and 40 wt% PVDF were examined. PVDF amount influences the morphology, diameter, and thermal stability of the fibers. Morphological results revealed that beadless PAN/PVDF nanofiber was obtained and the diameter of the PAN/PVDF nanofibers decreased with the increasing amount of PVDF. However, at 30 wt% beads formation on the fibers was begun to observe. Optimum conditions to obtain uniform and beadless PAN/PVDF nanofibers were determined as 20 wt% PVDF concentration. The air permeability tests of PAN/PVDF nanofibers containing 20 wt% PVDF indicated that these nanofibrous membranes are appropriate materials for air filtration applications.

1. Introduction

The electrospinning technique provides a convenient approach to produce continuous fibers with a diameter range of nano to micro-scale [1]. Electrospun nanofibers (NFs) are important nanomaterials with their large high porosity, specific surface area, small pore size, and well-connected pore structure [2]. Some of the potential application areas of the electrospun NFs are filtration membranes [3], drug delivery [4], tissue engineering [5, 6], catalysts [7], actuators [8], food packaging [9], etc.

In literature, electrospun nanofibrous membranes are reported among the attractive filter materials due to their high molecular orientation, excellent tensile strength [10], and thermal stability [11]. Filtration performances of nanofibrous membranes are higher compared to the traditional filtration materials such as glass fibers, spun-bonded fibers, and melt-blown fibers [12, 13]. In literature, various electrospun polymers have been examined as air filter membranes [13-15] and face masks [16, 17]. Polyacrylonitrile (PAN) which is a synthetic polymer having a semi-crystalline structure, is thermally stable and degrades over 300 °C [18]. PAN electrospun NFs are among the various materials which are widely utilized for filtration due to their unique thermal stability, superior mechanical properties, and good solvent resistance [19]. Bortolassi et al. studied antibacterial PAN nanofibrous membrane to remove air pollutants [15]. Three different particles were incorporated into PAN NFs: TiO_2, ZnO, and Ag, and the highest filtration efficiency was

*Corresponding author: atike.yardimci@usak.edu.tr
[a]orcid.org/0000-0001-5482-4230; [b]orcid.org/0000-0002-4581-2657; [c]orcid.org/0000-0001-9186-0978; [d]orcid.org/0000-0003-3598-0961; [e] orcid.org/0000-0001-7084-6253
DOI: http://dx.doi.org/10.17515/resm2022.357na1027

observed TiO_2 included PAN NFs with the smallest fiber diameter. PAN electrospun membranes were also examined for airborne fine-particle filtration by Al-Attabi et al [20]. Filtration efficiency and pressure drop of membranes were calculated from measurement of penetration through the membranes using KCl aerosol particles in the diameter range of 300 nm to 12 μm and separation efficiencies in the range of 73.8–99.78% was obtained for PAN NFs with an average diameter of 858 nm. This study indicated that electrospun membranes were appropriate materials for air filtration with their filtration stability at high air-flow rates.

PAN is a versatile polymer with high carbon content and it has been studied with many different polymers in the literature. Poly(methyl methacrylate) (PMMA) is widely acknowledged as a polymer with good elongation performance and it is one of the polymers used as a co-polymer of PAN in the electrospinning process [21]. PMMA finds use in transparent ait filter applications, but amorphous PMMA chains will irreversibly slide with one another during deformation and cause poor mechanical performance [22].

As a semi-crystalline polymer, PVDF is commonly used in ultrafiltration and microfiltration applications due to its excellent chemical resistance, thermal stability, high strength, and flexibility. Besides its advantages, the hydrophobic behavior of PVDF limits its applications. Therefore, to solve this problem, PVDF should be blended with a hydrophilic copolymer such as PAN, polyvinyl alcohol (PVA), poly(methyl methacrylate (PMMA) [23,24].

PAN/PVDF bicomponent NFs were utilized for different applications such as CO_2 capture [25], water filtration [26], adsorbent [27] for removing the dye in literature because of their appropriate structures to develop narrow microporous membranes [28]. Wang et al. studied hot pressed PAN/PVDF electrospun nanofibers for water ultrafiltration [26], they utilized DMF/aceton mixture to prepare PAN/PVDF solution.

In this study, we investigated the synthesis of PAN/PVDF bicomponent NFs by electrospinning method with different PVDF weight concentrations to develop beadless and low diameter PAN/PVDF nanofibrous membranes. The results showed that with increasing PVDF amount, the average diameter of NFs decreased, however, beads formation was observed on NFs at higher PVDF amounts. Therefore, the optimum PVDF ratio was found as 20 wt% for PAN/PVDF NFs with beadless and regular morphology. These nanofibrous membranes were tested for air permeability and found as a potential air filtration material.

2. Material and Method

2.1. Materials

PAN (MW=150.000), PVDF (MW ~180.000, Mn~ 71.000) and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich to produce bicomponent PAN/PVDF electrospun NFs.

2.2. Preparation of Electrospun PAN/PVDF NFs

For each solution, 0.41 g total polymer (PAN+PVDF) (8wt%) was dissolved in 5 ml DMF as a solvent. Firstly, PAN was dissolved in DMF by stirring for 1h at 60 ^oC on a magnetic stirrer, and then PVDF amounting to 10, 20, 30, and 40 wt% of the total polymer mass was inserted and subsequently, it was stirred for 3 h at 60 ^oC to obtain PAN/PVDF solutions.

The resultant PAN/PVDF solutions were filled into a 5 ml syringe connected to a high voltage supply capable of applying 40 kV for electrospinning process. For all experiments, the applied voltage was 15 kV and the flow rate of solution was kept at 1.5 μl/h. The Al foil covered collector was placed at a distance of 25 cm from the tip of the needle.

2.3. Characterization of Electrospun PAN/PVDF NFs

The morphology and diameter of PAN/PVDF NFs were characterized by Scanning electron microscopy (SEM, LEO 1430 VP). Prior to SEM examination, PAN/PVDF NFs on Al foil were cut in the scale of 1x1 cm-scale, and then samples were sputter-coated with gold to avoid charge accumulations. Coated samples were fixed onto metallic stubs with double-sided carbon tape and analyzed with a secondary-electron detector at an acceleration voltage of 20 kV. The thickness of nanofibrous films was measured by using cross-sectional SEM images of membranes.

Fourier-Transform Infrared Spectroscopy (FT-IR) characterizations of PAN/PVDF NFs were carried out between 450 and 4000 cm^{-1} wavenumbers with Perkin Elmer UATR Spectrum Two FT-IR. The resolution of FT-IR was 4 cm^{-1}. The number of scans collected was 4.

The thermal behavior of NFs was characterized by thermogravimetric analysis (TGA, Hitachi STA 7300) in the temperature range of 25-600 ^{o}C in a N_2 atmosphere at a heating rate of 10 ^{o}C /min.

The air permeability of the PAN/PVDF membrane was measured by an air permeability tester (Unitronics) at 25 ^{o}C and for a 50 mm diameter circular area. Air was sent to the sample with 100 Pa pressure for each test.

3. Results and Discussion

The morphology of electrospun PAN/PVDF bicomponent NF membranes was analyzed with SEM. SEM images indicated that as-collected PAN and PAN/PVDF electrospun nanofibres were morphologically uniform with a cylindrical shape (Fig. 1). Increasing PVDF content resulted in NFs with smaller diameters. The average diameter of electrospun neat PAN NFs was 348 nm (Table 1). After 10 wt% addition of PVDF, it decreased to 252 nm. The average NF diameter was measured as 246, 243, and 148 nm for 20%, 30%, and 40% PVDF ratios, respectively. Hakkah et al. also observed a decrease in fiber diameter with increasing PVDF concentration due to the decrease in solution viscosity [29]. PVDF At low PVDF concentration, the surface morphology of NFs was smooth. NFs were straight and randomly oriented and beadless formation was achieved up to 30 wt% PVDF content. Irregularities and beads were observed with increasing PVDF content they were clearly visible in Fig. 1. Therefore, the optimum PVDF concentration in PAN/PVDF electrospinning solutions was found to be 20 wt%. Dimethylformamide (DMF) was successfully used as a solvent for electrospinning processing of poly(acrylonitrile) [30] and in literature, generally, DMF was utilized to prepare PAN/PVDF electrospinning solutions[31,32]. However, Yalcinkaya et al. dissolved PVDF in dimethylacetamide (DMAc)/Acetone (4/1) mixture and PAN in DMF as a solvent [33]. Then, mixtures of two solutions were prepared using the 12% wt. PVDF and 8% wt. PAN at different weight ratios of PVDF/PAN. Contrary to our results, their results indicated that PVDF addition caused an increase in diameters of PAN nanofibers. This difference is due to the solvent difference in the PAN/PVDF solution.

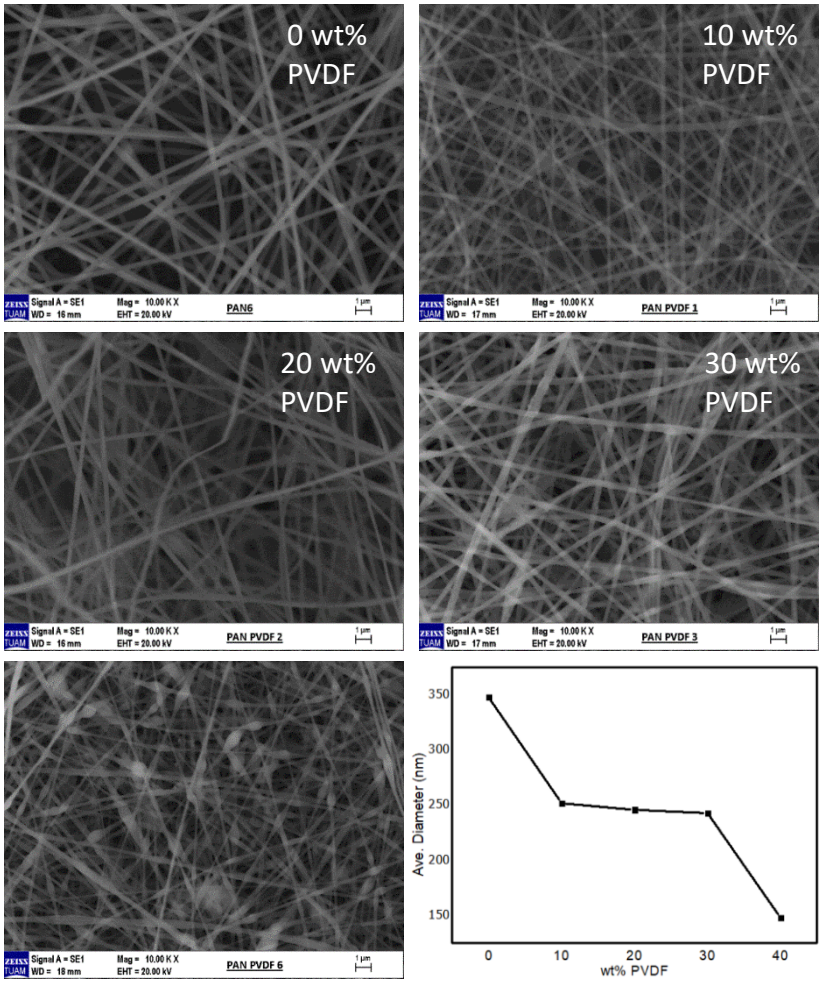


Fig. 1 SEM images of PAN/PVDF nanofibers containing different amounts of PVDF and average diameter vs. PVDF amount graph

Table 1. PAN/PVDF Bicomponent NFs with different PVDF weight concentrations and their average diameter values.

PAN (wt.%)	PVDF (wt.%)	Ave. Diameter (nm)
100	0	348
90	10	252
80	20	246
70	30	243
60	40	148

The structural properties of PAN/PVDF NFs containing different amounts of PVDF were characterized with FT-IR spectroscopy. The characteristic peaks of PAN around 2943 cm^{-1}, 2240 cm^{-1}, 1735 cm−1, and 1664 cm^{-1} were observed in Fig.2, assigned to the stretching vibrations of the –CH, –C≡N, –C=O, and –C=N groups, respectively [34]. The peak at 1454 cm^{-1} and 1068 cm-1 corresponded to the C=C and C-H. The characteristic peak of the nitrile groups stretching at 2240 cm^{-1} decreased dramatically with the increase of PVDF amount

similar to the reported in the literature [35]. For the samples containing a higher amount of PVDF NFs, the peak at 1405 and 1185 cm^{-1} is related to the symmetrical stretching of the $-CF_2$ group, which is a characteristic peak of PVDF and confirmed the PVDF existence in the PAN polymer mixture. C–F stretching vibration of the amorphous phase was also observed in FT-IR spectra of PAN/PVDF NFs at 880 cm^{-1} [36].

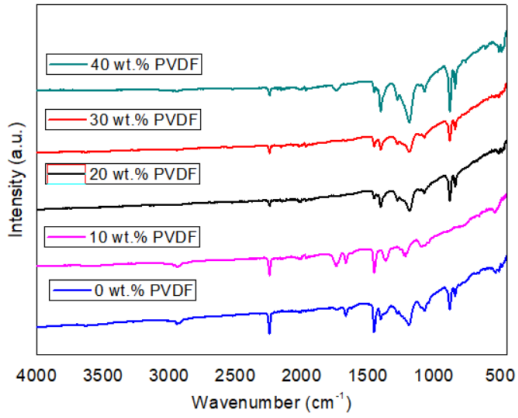


Fig. 2 FT-IR spectra of PAN/PVDF nanofibrous membranes containing different amounts of PVDF

Thermal analysis of PAN/PVDF nanofibrous membranes was carried out with TGA under N_2 atmosphere. A degradation step corresponded to the removal of water was observed at TGA graphs of PAN and PAN/PVDF NFs (Fig. 3) in the temperature range of 50-130 °C. Besides, the majority of the degradation of pure PAN NFs were carried out between 310-450 °C [37] while the decomposition temperatures of pure PVDF NFs in nitrogen atmosphere were at 450-480 °C [35]. The decomposition temperature of PAN/PVDF membranes containing different amounts of PVDF was found between the decomposition temperatures of PAN and PVDF and the degradation temperature of bicomponent nanofibres increased when the PVDF content increased in nanofibrous membranes. As a result, PVDF incorporation enhanced the thermal stability of PAN NFs.

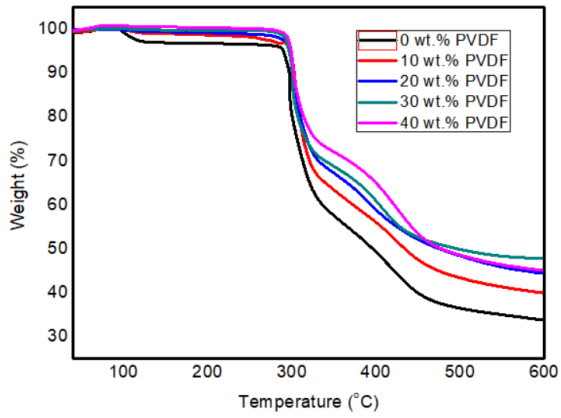


Fig. 3 TGA graphs of PAN/PVDF nanofibrous membranes containing different amounts of PVDF

According to SEM, FT-IR, and TGA results, 20 wt% PVDF concentration was found to be the optimum concentration for regular and beadless NF formation. Therefore, air permeability tests were performed for PAN/PVDF nanofibrous membranes containing 20 and 30 wt% PVDF concentrations and the membrane containing 20 wt% PVDF concentration gave an average air permeability value of 98 l/m2/s while the membrane containing 30 wt% PVDF concentration showed an average air permeability value of 143 l/m2/s under 100 Pa pressure. In literature, air permeability values of multi-layer PVDF-hexa-fluoropropylene (HPF) nanofibrous membranes under 100 Pa pressure were measured between 52.16-27.2 [38]. Their results indicated high air permeability, they proposed these nanofibrous multi-layer membranes for wound dressing and membrane distillation applications. In our study, obtained air permeability is higher than that obtained for PVDF/HPF NFs. Our results indicated that PAN/PVDF nanofibrous membranes produced in this study were suitable to utilize as air filter material with their high air permeability and good morphology.

4. Conclusions

In this study, beadless, regular and straight PAN and PAN/PVDF NFs were produced by the electrospinning method. These nanofibrous membranes were proposed for air filtration applications. The results indicated that the average diameter of the PAN/PVDF NFs decreased by increasing PVDF concentration in the electrospinning solution. High PVDF content caused bead formation and disordered NFs formation. Disordered sites and beads prevent a regular film formation and so weaken the mechanical properties of the obtained membrane. Therefore, for PAN/PVDF membranes 20 wt% PVDF was found to be the optimum amount for regular morphology based on SEM results.

The characteristic peaks of PAN were observed in FT-IR spectra, nitrile groups stretching decreased with the increasing amount of PVDF. For the samples containing a higher amount of PVDF, the symmetrical stretching of the $-CF_2$ group increased, which confirmed the PVDF existence in the NFs. When the thermal properties of NFs were analyzed, the decomposition of the membranes was carried out between the decomposition temperatures of PAN and PVDF. The degradation temperature increased with the increasing amount of PVDF in nanofibrous membranes. As a result, an enhancement of thermal stability was observed after PVDF incorporation.

Air permeability tests were applied to PAN/PVDF nanofibrous membrane containing 20 and 30 wt% PVDF and obtained average air permeability values indicated that electrospun nanofibrous PAN/PVDF membranes are appropriate to utilize in air filtration with their excellent morphological properties and air permeability results.

Acknowledgement

This work was supported financially by the Usak University Scientific Research Project (UBAP01 2021/MF001). The authors are very thankful to Scientific Analysis, Technological Application, and Research Center of Usak University for FT-IR measurements.

References

[1] Teo WE, Ramakrishna S. A review on electrospinning design and nanofibre assemblies. Nanotechnology, 2006; 17:14 R89. https://doi.org/10.1088/0957-4484/17/14/R01

[2] Bortolassi ACC, Nagarajan S, de Araújo Lima B, Guerra VG, Aguiar ML, Huon V, Soussan L, Cornu D, Miele P, Bechelany M. Efficient nanoparticles removal and bactericidal action of electrospun nanofibers membranes for air filtration. Materials Science and Engineering: C, 2019; 102: 718-729. https://doi.org/10.1016/j.msec.2019.04.094

[3] Patanaik, A, Jacobs V, Anandjiwala RD. Performance evaluation of electrospun nanofibrous membrane. Journal of Membrane Science, 2010; 352:1 136-142. https://doi.org/10.1016/j.memsci.2010.02.009
[4] Yu DG, Zhu LM, White K, Branford-White C. Electrospun nanofiber-based drug delivery systems. Health, 2009, 1:2 67. https://doi.org/10.4236/health.2009.12012
[5] Ince Yardimci A, Baskan O, Yilmaz S, Mese G, Ozcivici E, Selamet Y. Osteogenic differentiation of mesenchymal stem cells on random and aligned PAN/PPy nanofibrous scaffolds. Journal of biomaterials applications, 2019; 34:5 640-650. https://doi.org/10.1177/0885328219865068
[6] Ince Yardimci A, Aypek H, Ozturk O, Yilmaz S, Ozcivici E, Mese G, Selamet Y. CNT incorporated polyacrilonitrile/polypyrrole nanofibers as keratinocytes scaffold. in Journal of Biomimetics, Biomaterials and Biomedical Engineering. 2019. Trans Tech Publ. https://doi.org/10.4028/www.scientific.net/JBBBE.41.69
[7] Unnithan AR, Barakat NA, Nirmala R, Al-Deyab SS, Kim HY. Novel electrospun nanofiber mats as effective catalysts for water photosplitting. Ceramics International, 2012; 38:6 5175-5180. https://doi.org/10.1016/j.ceramint.2012.03.023
[8] Huang L, Xie X, Huang H, Zhu J, Yu J, Wang Y, Hu Z. Electrospun polyamide-6 nanofiber for hierarchically structured and multi-responsive actuator. Sensors and Actuators A: Physical, 2020; 302: 111793. https://doi.org/10.1016/j.sna.2019.111793
[9] Yardimci AI, Tarhan Ö. Electrospun Protein Nanofibers And Their Food Applications. Mugla Journal of Science and Technology. 6:2 52-62.
[10] Duan G, Fang H, Huang C, Jiang S, Hou H. Microstructures and mechanical properties of aligned electrospun carbon nanofibers from binary composites of polyacrylonitrile and polyamic acid. Journal of materials science, 2018; 53:21 15096-15106. https://doi.org/10.1007/s10853-018-2700-y
[11] Jiang S, Han D, Huang C, Duan G, Hou H. Temperature-induced molecular orientation and mechanical properties of single electrospun polyimide nanofiber. Materials Letters, 2018; 216: 81-83. https://doi.org/10.1016/j.matlet.2017.12.146
[12] Al-Attabi R, Dumée LF, Schütz JA, Morsi Y. Pore engineering towards highly efficient electrospun nanofibrous membranes for aerosol particle removal. Science of the total environment, 2018; 625: 706-715. https://doi.org/10.1016/j.scitotenv.2017.12.342
[13] Zhu M, Han J, Wang F, Shao W, Xiong R, Zhang Q, Pan H, Yang Y, Samal SK, Zhang F. Electrospun nanofibers membranes for effective air filtration. Macromolecular Materials and Engineering, 2017; 302:1 1600353. https://doi.org/10.1002/mame.201600353
[14] Matulevicius J, Kliucininkas L, Martuzevicius D, Krugly E, Tichonovas M, Baltrusaitis J. Design and characterization of electrospun polyamide nanofiber media for air filtration applications. Journal of nanomaterials, 2014. https://doi.org/10.1155/2014/859656
[15] Canalli Bortolassi AC, Guerra VG, Aguiar ML, Soussan L, Cornu D, Miele P, Bechelany M. Composites based on nanoparticle and pan electrospun nanofiber membranes for air filtration and bacterial removal. Nanomaterials, 2019; 9:12 1740. https://doi.org/10.3390/nano9121740
[16] Khandaker M, Progri H, Arasu DT, Nikfarjam S, Shamim N. Use of Polycaprolactone Electrospun Nanofiber Mesh in a Face Mask. Materials, 2021; 14:15 4272. https://doi.org/10.3390/ma14154272
[17] Zhang Z, Ji D, He H, Ramakrishna S. Electrospun ultrafine fibers for advanced face masks. Materials Science and Engineering: R: Reports, 2021; 143: 100594. https://doi.org/10.1016/j.mser.2020.100594
[18] Varshney K, Tayal N, Gupta U. Acrylonitrile based cerium (IV) phosphate as a new mercury selective fibrous ion-exchanger: synthesis, characterization and analytical applications. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1998; 145:1 71-81. https://doi.org/10.1016/S0927-7757(98)00657-8

[19] Hashmi M, Ullah S, Kim IS. Copper oxide (CuO) loaded polyacrylonitrile (PAN) nanofiber membranes for antimicrobial breath mask applications. Current Research in Biotechnology, 2019; 1: 1-10. https://doi.org/10.1016/j.crbiot.2019.07.001
[20] Al-Attabi R, Dumée LF, Kong L, Schütz JA, Morsi Y. High efficiency poly (acrylonitrile) electrospun nanofiber membranes for airborne nanomaterials filtration. Advanced Engineering Materials, 2018, 20:1 1700572. https://doi.org/10.1002/adem.201700572
[21] Hong CK, Yang KS, Oh SH, Ahn JH, Cho BH, Nah C. Effect of blend composition on the morphology development of electrospun fibres based on PAN/PMMA blends. Polymer International, 2008; 57: 1357 - 1362. https://doi.org/10.1002/pi.2481
[22] Lv S, Zhao X, Shi L, Zhang G, Wang S, Kang W, Zhuang X. Preparation and Properties of sc-PLA/PMMA Transparent Nanofiber Air Filter. Polymers, 2018; 10:9 996. https://doi.org/10.3390/polym10090996
[23] Cao X, Ma J, Shi X, Ren Z. Effect of TiO2 nanoparticle size on the performance of PVDF membrane. Applied Surface Science, 2006; 253:4 2003-2010. https://doi.org/10.1016/j.apsusc.2006.03.090
[24] Li N, Xiao C, An S, Hu X. Preparation and properties of PVDF/PVA hollow fiber membranes. Desalination, 2010; 250:2 530-537. https://doi.org/10.1016/j.desal.2008.10.027
[25] Heo YJ, Zhang Y, Rhee KY, Park SJ. Synthesis of PAN/PVDF nanofiber composites-based carbon adsorbents for CO2 capture. Composites Part B: Engineering, 2019; 156: 95-99. https://doi.org/10.1016/j.compositesb.2018.08.057
[26] Wang Z, Sahadevan R, Crandall C, Menkhaus TJ, Fong H. Hot-pressed PAN/PVDF hybrid electrospun nanofiber membranes for ultrafiltration. Journal of Membrane Science, 2020; 611: 118327. https://doi.org/10.1016/j.memsci.2020.118327
[27] Mokhtari-Shourijeh Z, Langari S, Montazerghaem L, Mahmoodi NM. Synthesis of porous aminated PAN/PVDF composite nanofibers by electrospinning: Characterization and Direct Red 23 removal. Journal of Environmental Chemical Engineering, 2020. 8(4): 103876. https://doi.org/10.1016/j.jece.2020.103876
[28] Lee SY, Park SJ. Effects of CO2 activation on electrochemical performance of microporous carbons derived from poly (vinylidene fluoride). Journal of Solid State Chemistry, 2013; 207: 158-162. https://doi.org/10.1016/j.jssc.2013.09.013
[29] Hakkak F, Rafizadeh M, Sarabi AA, Yousefi M. Optimization of ionic conductivity of electrospun polyacrylonitrile/poly (vinylidene fluoride)(PAN/PVdF) electrolyte using the response surface method (RSM). Ionics, 2015; 21: 1945-1957. https://doi.org/10.1007/s11581-014-1363-1
[30] Wannatong L, Sirivat A, Supaphol P. Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene. Polymer International, 2004; 53:11 1851-1859. https://doi.org/10.1002/pi.1599
[31] Mokhtari-Shourijeh, Z, Langari S, Montazerghaem L, Mahmoodi NM. Synthesis of porous aminated PAN/PVDF composite nanofibers by electrospinning: Characterization and Direct Red 23 removal. Journal of Environmental Chemical Engineering, 2020; 8:4 103876. https://doi.org/10.1016/j.jece.2020.103876
[32] Heo YJ, Zhang Y, Rhee KY, Park SJ. Synthesis of PAN/PVDF nanofiber composites-based carbon adsorbents for CO2 capture. Composites Part B: Engineering, 2019; 156: 95-99. https://doi.org/10.1016/j.compositesb.2018.08.057
[33] Yalcinkaya F, Yalcinkaya B, Pazourek A, Mullerova J, Stuchlik M, Maryska J. Surface modification of electrospun PVDF/PAN nanofibrous layers by low vacuum plasma treatment. International Journal of Polymer Science, 2016. https://doi.org/10.1155/2016/4671658
[34] Chen L, Bromberg L, Schreuder-Gibson H, Walker J, Hatton TA, Rutledge GC. Chemical protection fabrics via surface oximation of electrospun polyacrylonitrile fiber mats.

Journal of Materials Chemistry, 2009; 19:16 2432-2438. https://doi.org/10.1039/b818639a

[35] Yalcinkaya F, Yalcinkaya B, Pazourek A, Mullerova J, Stuchlik M, Maryska J. Surface modification of electrospun PVDF/PAN nanofibrous layers by low vacuum plasma treatment. International Journal of Polymer Science, 2016. https://doi.org/10.1155/2016/4671658

[36] Merlini C, de Oliveira Barra GM, da Silva Ramôa SDA, Contri G, dos Santos Almeida R, d'Ávila MA, Soares BG. Electrically conductive polyaniline-coated electrospun poly (vinylidene fluoride) mats. Frontiers in Materials, 2015; 2: 14. https://doi.org/10.3389/fmats.2015.00014

[37] Duan Q, Wang B, Wang H. Effects of stabilization temperature on structures and properties of polyacrylonitrile (PAN)-based stabilized electrospun nanofiber mats. Journal of Macromolecular Science, Part B, 2012; 51:12 2428-2437. https://doi.org/10.1080/00222348.2012.676415

[38] Yan-Qing L, Jia-Wen F, Cheng-Cheng Z, Yue T, Zhi L, JiHuan H. Air Permeability of Nanofiber Membrane with Hierarchical Structure. Thermal Science, 2018; 22:4 1637-1643. https://doi.org/10.2298/TSCI1804637L