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Mechanical Properties Of Nylon 6,6 Nanofiber Membranes

Nylon 6,6 Nanolif Membranların Mekanik Özelliklerinin İncelenmesi

Meltem YANILMAZ

Istanbul Technical University, Faculty of Textile Technology and Design, Istanbul, Turkey

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Sorumlu Yazara ait Orcid Numarası (Corresponding Author's Orcid Number) :

<https://orcid.org/0000-0003-0562-5715>



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**MECHANICAL PROPERTIES OF NYLON 6,6
NANOFIBER MEMBRANES**

Meltem YANILMAZ*

Istanbul Technical University, Faculty of Textile Technology and Design, Istanbul, Turkey

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ABSTRACT: Nylon 6,6 nanofiber membranes were produced by electrospinning technique and mechanical properties of the nylon 6,6 membranes prepared with different solvent systems were investigated. Nylon 6,6 solutions were prepared by dissolving nylon 6,6 in the solvent system of formic acid/trifluoroethyl alcohol with the ratios of 50/50, 75/25 and 100/0 (v/v). Results showed that solvent type has a pronounced effect on average fiber diameters and mechanical properties. Increasing formic acid led to lower average fiber diameters and enhanced mechanical strength. The nylon 6,6 membrane prepared by using formic acid exhibited the tensile strength of about 20 MPa with the average fiber diameter of about 400 nm.

Keywords: Nylon 6,6, electrospinning, nanofibers

**NYLON 6,6 NANOLİF MEMBRANLARIN
MEKANİK ÖZELLİKLERİNİN İNCELENMESİ**

ÖZET: Çalışmada naylon 6,6 nanolif membranlar elektroğirme tekniği ile üretilmiştir ve değişik çözücü sistemleri ile üretilmiş nylon 6,6 nanolif membranların mekanik özellikleri incelenmiştir. Naylon 6,6 çözeltileri naylon 6,6 nın formik asit/trifloroetil alkol çözücü sisteminde 50/50, 75/25 ve 100/0 oranlarında çözünmesiyle hazırlanmıştır. Sonuçlar çözücü tipinin ortalama nanolif çaplarında ve mekanik özelliklerde belirgin etkisi olduğunu göstermiştir. Formik asit artışı düşük nanolif çaplarına ve artan mekanik mukavemete neden olmuştur. Formik asit kullanılarak hazırlanan membran 400 nm ortalama nanolif çapı ile 20MPa civarı mukavemet göstermiştir.

Anahtar Kelimeler: Naylon 6,6, elektroğirme yöntemi, nanolifler

Sorumlu Yazar/Corresponding Author: yanilmaz@itu.edu.tr <https://orcid.org/0000-0003-0562-5715>

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1. INTRODUCTION

Electrospinning is a widely used technique to produce nanofibers and characteristics of nanofibers including small diameter and extremely high surface area to volume ratio makes these nano-sized fibers good candidates for many application areas such as separators, electrodes, filtration, tissue engineering, wound dressing, etc [1-4]. Electrospinning technique relies on application of high voltage on polymer solution. Polymer solution is fed to the needle tip and solution droplet turns into conical shape (Taylor cone) under electric field. When critical voltage is reached polymeric jets are formed and move to the collector. Under the influence of electrical field, jets get thinner, solvent evaporates and nano-sized fibers are formed on the collector [5-7].

Process and solution parameters including solution composition, polymer solution feed rate, applied voltage, and distance between tip and the collector affect average nanofiber diameters [8]. In general, as the applied voltage increases above the critical value, the nanofiber diameter decreases and then increases after a definite point. As the flow rate increases, the nanofiber diameter increases. At a high polymer concentration, the viscoelastic force resists the stretching repulsive forces of charge and leads to an increase in nanofiber diameter. An increase in the distance between the capillary and the collector results in decreased diameters [9].

Solvent type is one of the most important parameter that affects the morphology and properties of nanofiber membranes [10-12]. Jarusuwannapoomv et al. [13] studied eighteen different solvents to dissolve and electrospin polystyrene. It was reported that dipole moment, conductivity, boiling point, viscosity and surface tension of the solutions are important factors to determine the electrospinnability [13]. An increase in average fiber diameters with increased TFE ratio for gelatin/acetic acid/TFE system was reported by Choktaweasap et al. [14]. The result was attributed to greater viscosity of the solvents by increasing TFE ratio. Mit-uppatham [15] et al. investigated nylon 6 in formic acid and m-cresol solvent system and significant change in morphology was observed when the content of m-cresol was increased owing to the changes in solution properties [15].

Mechanical, chemical and thermal stability of nanofiber membranes are critical properties that affect the performance of nanofiber membranes for many applications especially battery separation, filtration, protective clothing, sensors, composite reinforcement and biomedical applications [16-19]. Polyacrylonitrile, polyvinylidene fluoride, polymethyl metacrylate, polyethylene oxide, polyvinylalcohol, polyurethane, etc. have been commonly used for fabrication nanofiber membranes. However, mechanical properties of these electrospun nanofiber membranes are limited and mechanical strength of electrospun membranes can be enhanced by using polymers with higher mechanical strength such as nylon 6,6 [20]. Nylon 6, 6 nanofibers have been preferred due to their high mechanical strength and high thermal stability [16, 19, 21-25].

Formic acid and trifluoroethyl alcohol are the most commonly used solvents for electrospinning of nylon based polymers [22, 24, 26]. The solvent systems for different polymers including polycaprolactone [27-29], cellulose acetate [30-32], polymethylsilsesquioxane [33], polystyrene [13], polyurethane [34], polylactic acid [11, 35], poly(ethylene oxide) [10], nylon 6 [36], polymethylmetacrylate [37] have been reported. However, to the best of our knowledge, the effect of different solvent system on the morphology and mechanical properties of nylon6,6 nanofiber membrane has not been reported so far. In this study, different solvent systems were utilized to prepare nylon 6,6 nanofiber membranes. Morphological and mechanical properties of these membranes were examined in order to investigate the effect of solvent system on the performance of nylon 6,6 nanofiber membranes.

2. MATERIALS AND METHODS

Nylon 6,6, formic acid (FA), and trifluoroethyl alcohol (TFE) were purchased from Aldrich. All chemicals were used as received without further purification. Nylon 6,6 solutions were prepared by dissolving 18 wt % nylon 6,6 in formic acid/trifluoroethyl alcohol with the ratios of 50/50, 75/25 and 100/0 (vol/vol). The solutions were stirred for 12 hours to dissolve the polymer. During electrospinning process, a high voltage of 20 kV was provided. The feeding rate used was 1 ml/h and the tip-to-collector-distance was 11 cm. In order to determine average fiber diameters, the SEM images were analyzed by using Revolution software and 100 measurement were used for each specimen. The mechanical properties of the membranes were determined by using a universal tensile tester with 100 N capacity load cell. The thicknesses were measured by using a digital micrometer. The extension rate was 10 mm/min at room temperature and at least 5 specimens with the average thickness of 40 μm were tested for each specimen. The procedure has been known as Huang's [38] method and has been commonly used for nanofiber membranes in the literature [16, 26, 38].

3. RESULTS AND DISCUSSION

SEM images and fiber diameter distributions of the nylon 6,6 nanofiber membranes are presented in Figure 1. For all studied solvent systems (formic acid/trifluoroethyl alcohol with the ratios of 50/50, 75/25 and 100/0 (vol/vol)), uniform fiber morphology was observed and increasing FA content led to thinner fiber diameters. Table 1 shows the average fiber diameters with respect to solvent systems. When 50/50 FA/TFE was used, average fiber diameters were reported as 3007 nm. Increasing FA content to 75% led to a decrease in average fiber diameters, 2234 nm. When only FA was used, the average fiber diameter was reported as 399 nm. The dielectric constant of solvent system is one of the most important factor which affects the electrospinnability, morphological appearance, and average fiber diameters [12, 28]. The significant decrease in average fiber diameter could be explained by dielectric properties of the

solvents. The dielectric constant of TFE is 8.55 whereas that of formic acid is 58.5 [14, 31]. Due to the high dielectric constant of formic acid, average nanofiber diameters decreased. Similar results were observed in earlier studies. Nirmala et al. [36] investigated different solvents, formic acid, dichloromethane, acetic acid, chlorophenol, hexafluoroisopropanol, and

trifluoroacetic acid, and reported that when formic acid was used, the thinnest fibers were observed. The result was attributed to dielectric constant of the solvent. The electrospinning of polymer from highly polar solvents led to smaller fiber diameters [36].

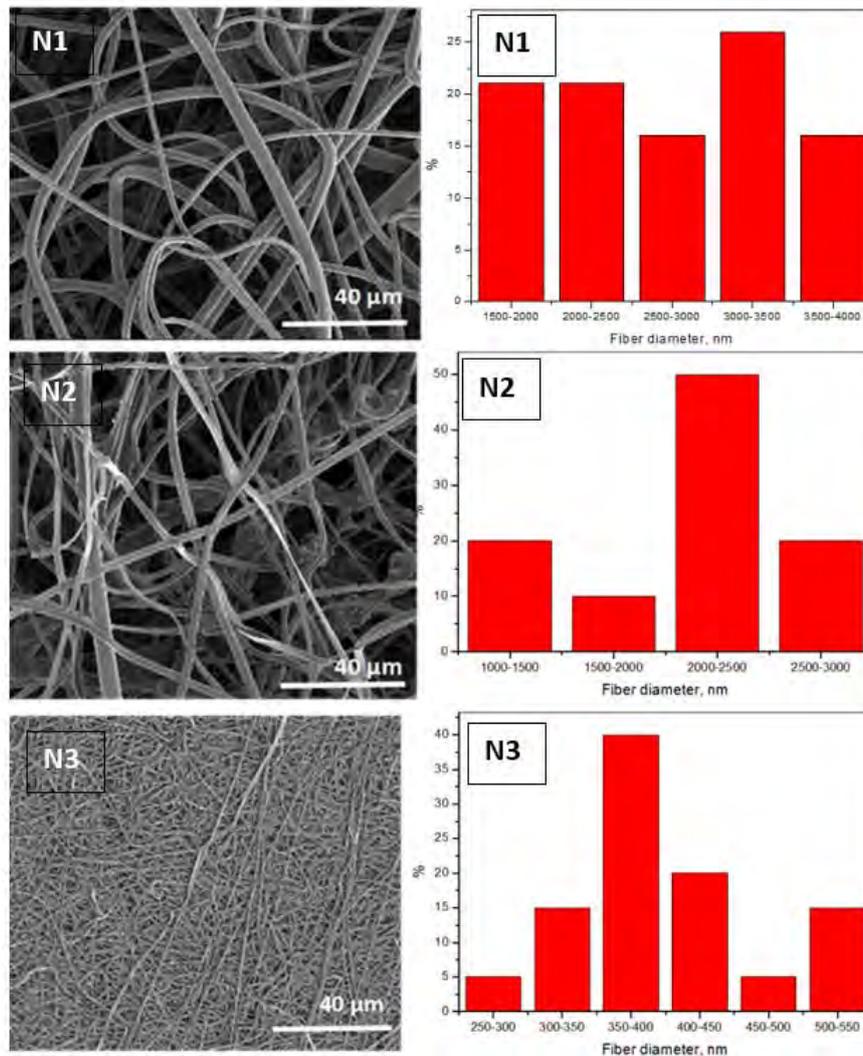


Figure 1 SEM images of nylon 6,6 nanofibers prepared with FA/TFE with the ratios of 50/50 (N1), 75/25 (N2) and 100/0 (N3).

Table 1 Sample properties

Samples	Short form	Concentration	Formic acid/ Trifluoroethyl alcohol	Average fiber diameter (nm)
Nylon 6,6	N1	18%	50/50	3007±990
Nylon 6,6	N2	18%	75/25	2234±422
Nylon 6,6	N3	18%	100/0	399±74

The main factors that affect the mechanical properties of nanofibers are fiber structure, arrangement of fiber, single fiber properties and interaction between fibers. Figure 2 and 3 show the stress strain curves of nylon 6,6 nanofiber membranes. The nylon 6,6 nanofiber membranes prepared with FA/TFE (50/50 and 75/25 vol/vol), showed the strength of about 0.5 MPa. When only formic acid was used, the strength was increased to about 25 MPa. This increase could be attributed to the morphology of the resultant membranes. The higher strength with decreasing fiber diameter could be explained by larger contact area and high cohesive force. More fiber cohesion with decreasing fiber diameter resulted in higher strength. Huang et al. [38] also studied the mechanical properties of gelatin nanofibers and enhanced strength was explained by higher cohesive force resulted from decreased average fiber diameters. Baji et al. [39] also studied the mechanical properties of nanofibers and reported an increase in strength as the average fiber diameter decreased. Increased strength was attributed to dense packing and higher orientation [39]. Maleki et al. [11] studied different solvent type on the morphology and mechanical properties of electrospun poly(L-lactide). Higher strength with decreased fiber diameters was reported and explained by larger contact area between fibers [11]. Even the strength value changed significantly with different solvent systems, all membranes studied showed similar strain value which was about 0.5.

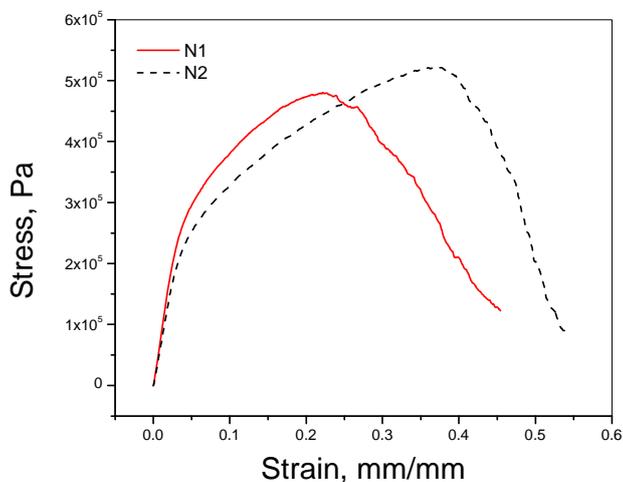


Figure 2. Stress strain curve of nylon 6,6 nanofiber membrane prepared with FA/TFE with the ratios of 50/50 (N1) and 75/25 (N2).

Figure 4 shows the FTIR spectra of nylon 6,6 nanofibers. The characteristic peaks of nylon 6,6 were observed for all membranes. Free N—H axial deformation was seen at ~ 3300 cm^{-1} . CH_2 -NH axial deformations were seen at about 2936 and 2862 cm^{-1} . The peaks at about 1636 and 1537 cm^{-1} belonged to C=O axial deformation, amide I and C—N axial deformation and CO—N—H angular deformation, amide II, respectively [19, 40]. Since solvent system was completely evaporated after

electrospinning, same characteristic peaks were observed from the spectra of nylon 6,6 nanofiber membranes prepared by different solvent systems.

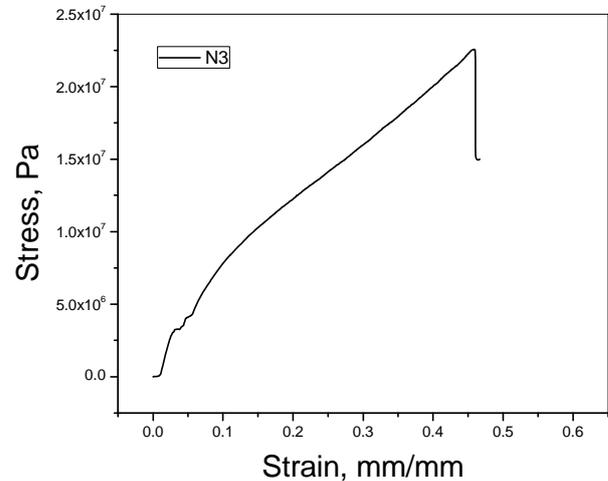


Figure 3. Stress strain curve of nylon 6,6 nanofiber membrane prepared with FA (N3)

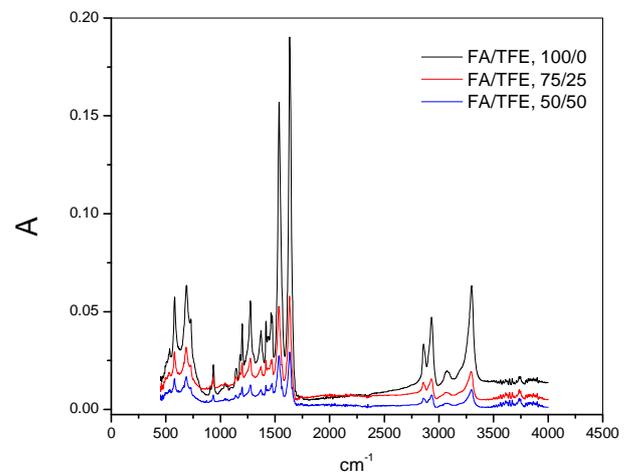


Figure 4 FTIR spectra of nylon 6,6 nanofibers.

4. CONCLUSIONS

Mechanical performance of nanofiber membranes limits their application and the solvent type is critical factor to determine the morphology and performance of nanofiber membranes. In this study, nylon 6,6 nanofiber membranes were prepared by using FA/TFE system with different ratios for the first time. The effect of solvent type on the morphology and mechanical properties was studied. It was observed that solvent type influence the strength and average fiber diameters significantly. Nylon 6,6 nanofiber membranes prepared with formic acid showed the highest strength with thinnest fiber diameters.

REFERENCES

1. Ayaz O, Uçar N, Bahar E., Oksuz M., Ucar M., Onen A., Demir A., Wang Y. (2012), "Production And Analysis of Composite Nanofiber And Heat Applied Nanofiber". *Tekstil ve Mühendis*, 19(85) 6-9.
2. Çallıoğlu, F.C. and Jirsak O. (2013), "The Effect of Polymer and Salt Concentration on Fiber Properties in Electrospinning of Polyurethane Nanofibers" *Tekstil ve Mühendis*, 20 (90) 1-6.
3. Lee, H., et al., (2014), A review of recent developments in membrane separators for rechargeable lithium-ion batteries. *Energy & Environmental Science*, 7(12), 3857-3886.
4. Zhang, X., et al. (2011), *Electrospun nanofiber-based anodes, cathodes, and separators for advanced lithium-ion batteries*. *Polymer Reviews*, 51(3) 239-264.
5. Erdem, R. and Erdem, Ö., (2017), *Investigation the Morphological and Luminescence Properties of Ligand Doped Polyurethane Nanofibers Produced by Electrospinning*. *Tekstil ve Mühendis* 24 (105), 18-24.
6. Pant, H.R., et al. (2010), *Effect of successive electrospinning and the strength of hydrogen bond on the morphology of electrospun nylon-6 nanofibers*. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 370(1-3), p. 87-94.
7. Bagheri, H. and Aghakhani A. (2012), *Polyaniline-nylon-6 electrospun nanofibers for headspace adsorptive microextraction*. *Analytica chimica acta*, 713, 63-69.
8. Beachley, V. and Wen X., (2009) *Effect of electrospinning parameters on the nanofiber diameter and length*. *Materials Science and Engineering: C*, 29(3), 663-668.
9. Pillay, V., et al., (2013), A review of the effect of processing variables on the fabrication of electrospun nanofibers for drug delivery applications. *Journal of Nanomaterials*.
10. Son, W.K., et al., (2004), *The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly (ethylene oxide) fibers*. *Polymer*, 45(9), 2959-2966.
11. Casasola, R., et al., (2014), *Electrospun poly lactic acid (PLA) fibres: effect of different solvent systems on fibre morphology and diameter*. *Polymer* 55(18), 4728-4737.
12. Chuangchote, S., Sagawa T., and Yoshikawa S., (2009), *Electrospinning of poly (vinyl pyrrolidone): Effects of solvents on electrospinnability for the fabrication of poly (p-phenylene vinylene) and TiO2 nanofibers*. *Journal of applied polymer science*, 114(5), 2777-2791.
13. Jarusuwannapoom, T., et al., (2005), *Effect of solvents on electrospinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers*. *European Polymer Journal*, 41(3), 409-421.
14. Choktaweasap, N., et al. (2007), *Electrospun gelatin fibers: effect of solvent system on morphology and fiber diameters*. *Polymer Journal*, 39(6), 622-631.
15. Mit-uppatham, C., Nithitanakul M., and Supaphol P., (2004), *Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter*. *Macromolecular Chemistry and Physics*, 205(17), 2327-2338.
16. Yanilmaz, M., Dirican M., and Zhang X, (2014). *Evaluation of electrospun SiO 2/nylon 6, 6 nanofiber membranes as a thermally-stable separator for lithium-ion batteries*. *Electrochimica Acta*, 133, 501-508.
17. Pant, H.R., et al., (2011), *Electrospun nylon-6 spider-net like nanofiber mat containing TiO2 nanoparticles: a multifunctional nanocomposite textile material*. *Journal of hazardous materials*, 185(1), 124-130.
18. Palazzetti, R., Zucchelli A., and Trendafilova I., (2013), *The self-reinforcing effect of Nylon 6, 6 nano-fibres on CFRP laminates subjected to low velocity impact*. *Composite Structures*, 106, 661-671.
19. Shrestha, B.K., et al., (2016), *Development of polyamide-6, 6/chitosan electrospun hybrid nanofibrous scaffolds for tissue engineering application*. *Carbohydrate Polymers*, 148,107-114.
20. Yanilmaz, M., et al., (2017), *High-strength, thermally stable nylon 6, 6 composite nanofiber separators for lithium-ion batteries*. *Journal of Materials Science*, 52(9), 5232-5241.
21. Matulevicius, J., et al., (2016), *The comparative study of aerosol filtration by electrospun polyamide, polyvinyl acetate, polyacrylonitrile and cellulose acetate nanofiber media*. *Journal of Aerosol Science*, 92, 27-37.
22. Huang, L. and McCutcheon J.R., (2014) *Hydrophilic nylon 6, 6 nanofibers supported thin film composite membranes for engineered osmosis*. *Journal of membrane science*, 457, 162-169.
23. Jeong, J., et al., (2006), *Fabrication of MWNTs/nylon conductive composite nanofibers by electrospinning*. *Diamond and related materials*, 15 (11-12), 1839-1843.
24. Choi, J., et al., (2010), *MWCNT-OH adsorbed electrospun nylon 6, 6 nanofibers chemiresistor and their application in low molecular weight alcohol vapours sensing*. *Synthetic Metals*, 160 (23-24), 2664-2669.
25. Navarro-Pardo, F., et al., (2013), *Effects on the thermo-mechanical and crystallinity properties of nylon 6, 6 electrospun fibres reinforced with one dimensional (1D) and two dimensional (2D) carbon*. *Materials*, 6(8), 3494-3513.
26. Li, Y., Huang Z., and Lü Y., (2006), *Electrospinning of nylon-6, 66, 1010 terpolymer*. *European polymer journal*, 42(7), 1696-1704.
27. Van der Schueren, L., et al., (2011), *An alternative solvent system for the steady state electrospinning of polycaprolactone*. *European Polymer Journal*, 47(6),1256-1263.
28. Lee, K., et al., (2003), *Characterization of nano-structured poly (ϵ -caprolactone) nonwoven mats via electrospinning*. *Polymer*, 44(4), 1287-1294.
29. Shawon, J. and Sung C., (2004) *Electrospinning of polycarbonate nanofibers with solvent mixtures THF and DMF*. *Journal of materials science*, 39(14), 4605-4613.
30. Han, S.O., et al., (2008), *Electrospinning of cellulose acetate nanofibers using a mixed solvent of acetic acid/water: Effects of solvent composition on the fiber diameter*. *Materials Letters*, 62(4-5), 759-762.
31. Tungprapa, S., et al., (2007), *Electrospun cellulose acetate fibers: effect of solvent system on morphology and fiber diameter*. *Cellulose*, 14(6),563-575.
32. Celebioglu, A. and Uyar T., (2011), *Electrospun porous cellulose acetate fibers from volatile solvent mixture*. *Materials Letters*, 65(14), 2291-2294.
33. Luo, C., Nangrejo M., and Edirisinghe M., (2010), *A novel method of selecting solvents for polymer electrospinning*. *Polymer*, 51(7), 1654-1662.

34. Erdem, R., et al., (2015), *The impact of solvent type and mixing ratios of solvents on the properties of polyurethane based electrospun nanofibers*. Applied Surface Science, 2015. 334: p. 227-230.
35. Qi, Z., et al., (2009), *Highly porous fibers prepared by electrospinning a ternary system of nonsolvent/solvent/poly (l-lactic acid)*. Materials Letters, 63(3-4), 415-418.
36. Nirmala, R., et al., (2010), *Effect of solvents on high aspect ratio polyamide-6 nanofibers via electrospinning*. Macromolecular research, 18(8), 759-765.
37. Qian, Y.-F., et al., (2010), *Electrospinning of polymethyl methacrylate nanofibres in different solvents*. 2010.
38. Huang, Z.-M., et al., (2004), *Electrospinning and mechanical characterization of gelatin nanofibers*. Polymer, 45(15), 5361-5368.
39. Baji, A., et al., (2010), *Electrospinning of polymer nanofibers: effects on oriented morphology, structures and tensile properties*. Composites science and technology, 70(5), 703-718.
40. Abbasi, A., et al., (2014), *Electrospinning of nylon-6, 6 solutions into nanofibers: rheology and morphology relationships*. Chinese Journal of Polymer Science, 32(6), 793-804.