Journal of Materials Sciences and Applications
2018; 4(5): 68-74
http://www.aascit.org/journal/jmsa
ISSN: 2381-0998 (Print); ISSN: 2381-1005 (Online)

American Association for Science and Technology

Electrospinning of Polyacrylonitrile Nanofiber Membrane for Bacteria Removal

Veereshgouda Shekharagouda Naragund, Prasanta Kumar Panda*

Materials Science Division, CSIR–National Aerospace Laboratories, Bengaluru, India

Email address

pkpanda@nal.res.in (P. K. Panda)
*Corresponding author

Citation

Veereshgouda Shekharagouda Naragund, Prasanta Kumar Panda. Electrospinning of Polyacrylonitrile Nanofiber Membrane for Bacteria Removal. *Journal of Materials Sciences and Applications.* Vol. 4, No. 5, 2018, pp. 68-74.

Received: November 17, 2018; **Accepted**: November 27, 2018; **Published**: December 19, 2018

Abstract: Electrospinning is a popular method to obtain nanofibers. Polyacrylonitrile (PAN) nanofibers in the range of 50 to 750 nm were prepared by electrospinning of homogeneous viscous solutions with varied polymer concentration in 10 – 16% (w/v) range in N, N- Dimethylformamide (DMF). The morphology of fibers observed by Scanning Electron Microscopy (SEM) indicated that the morphology transformation from beaded fiber to cylindrical form occurred at 14%, and the average fiber diameter at this concentration is 379 ± 54 nm. The polyacrylonitrile nanofibers were characterized by the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR). Differential Scanning Calorimeter (DSC) study of electrospun fibers revealed the presence of three thermal transitions in glass transition of PAN fibers. Membrane of 14% PAN nanofiber was subjected to vacuum for removal of air from the pores along with partial densification. This membrane was tested for bacteria reduction and found to eliminate model *E. coli* bacteria up to 99.9997%. In addition, membranes of different thicknesses in the range of 125 µm to 750 µm were also electrospun and flow rate of water (flux) was measured. It was found that the flux exponentially decreased with the increase in thickness due to the strong resistance to flow through nanosized pores.

Keywords: Polymer Membranes, Electrospinning, Nanofibers, Bacteria Removal, Vacuum Process

1. Introduction

Water pollution is a major challenge that is faced by countries worldwide and especially in developing countries such as India and China which have high population. Different types of contaminants can be present in water. They can vary from micro to nano-particles [1, 2], disease causing bacteria [3-6], toxic metal ions [7], dyes [8] and other chemicals such as herbicides [9]. Removal of particulates and bacteria is a challenge due to small size of these contaminants that require small pore sizes restricting water flux. Many methods of filtration such as non-woven membranes [10], activated carbon filters [11, 12], reverse osmosis (RO) membranes [13], and UV radiation [14] are used to reduce the particulates and killing bacteria with varied degree of reduction efficiency and flux rates. Recently, membranes prepared by electrospinning technique are found to simultaneously reduce particulates and bacteria simultaneously with higher flux rates [6].

Electrospinning is a popular method to obtain high aspect ratio sub-micro and nanofibers in the form of non-woven membranes/ sheets [15, 16]. Many polymers as well as ceramics have been processed [17, 18]. In this technique, a high voltage is applied to polymer solutions/melts carried through a metallic capillary such as syringe needle [18, 19]. When the applied voltage is above a critical voltage, a fine jet is ejected from droplet found at the edge of the capillary needle. The jet subdivides into thousands of nanofibers and deposits as a membrane over a metallic collector connected to neutral or negative of high voltage source. After certain deposition time, a thick, free standing membrane can be peeled off from the collector. The membranes are suitable for wide variety of applications such as in filtration of water [1-8] and air [20], drug delivery and scaffolds for tissue growth in biomedical field [21, 22], protective clothing [23, 24] due to their novel properties such as large specific surface area and high open porosity between the fibers.

Many techniques have been applied to increase the membrane strength and bacterial reduction of nanofiber membranes such as addition of high cost material such as CNT and biocides into the spinning solution [25, 26]. The biocides or other chemicals incorporated into the nanofibers may be released into water negatively affecting water taste/quality and in long term health of a person [27]. It may be noted that studies are conducted on very thin (<200 μm) membrane [1, 3, 6]. At this thickness electrospun membranes can get damaged while handling, effectively decreasing filtration capability in practical application. Therefore, there is need to use thicker membranes for the filters.

Polyacrylonitrile is a suitable polymer for water filtration membranes due to its hydrophilic nature, chemical and thermal stability and possibility of wide range applications therefore, it is chosen as the polymer in this study. Many have reported the electrospinning of PAN [23, 24, 28]. It is observed in literature that the electrospun membranes are highly porous and puffy but there is no control of porosity of the deposited nanofibers.

In this paper, attempts have been made to prepare PAN membrane filter using electrospinning technique and to study the bacteria reduction efficiency using *E. Coli* as model organism. In addition, the membranes of different thicknesses prepared and the flow rate of water (flux) was measured.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, white powder, Mw=150,000) purchased from M/s Sigma Aldrich. N, N-Dimethylformamide (DMF) was procured from M/s. SDFCL, India used as solvent. Polypropylene (PP) cloth was sourced from local suppliers.

2.2. Preparation of Solution and Electrospinning of PAN Nanofiber

10-16% (w/v) PAN solutions were prepared using DMF as solvent. Briefly, 1g, 1.2g, 1.4g, and 1.6g of PAN powder dissolved in 10ml DMF. Homogeneous viscous liquid was obtained after about 8h magnetic stirring at room temperature. The PAN solution preparation and electrospinning conditions are summarized in Table 1.

Table 1. *PAN solution preparation and electrospinning conditions.*

Chemical precursor	Preparation of solution	Electrospinning conditions
(i) Polyacrylonitrile (PAN) (Mw=1,50,000) (ii) Dimethylformamide (DMF)	10-16% (w/v) PAN in 10 ml DMF at room temperature with constant stirring for 8h. Solution was used next day after stirring again for 1h.	(i) Needle: 24 Gauge, 0.55 mm outer diameter; (ii) Tip to collector distance (TCD): 14 cm; (iii) DC Voltage: 17 to 19 kV; (iv) Flow rate: 1.7 ml/h (v) Humidity: 75-85%

The electrospinning unit was supplied by M/s. E-spin Nanotech, Kanpur, India. The schematic diagram of electrospinning setup is presented in Figure 1. In electrospinning, the PAN solution was carefully filled into a 5 ml syringe fitted with metallic capillary needle (24G). A horizontally movable plate (15 × 21.5 cm^2) warped with aluminum foil (0.05 mm thick) was used to collect the fibers. Samples were electrospun for about 15 to 20 min. for the observation under SEM. For membrane preparation, the electrospinning was carried out for 32 h. The resulting membrane had an average thickness of 3.5 ± 0.35 mm was stored in air tight compartment. Similarly, membranes of thickness in the range of 125 to 750 μm were also prepared for water flow rate (flux) determination by varying the electrospinning time. The flow-sheet procedure to fabricate the filter membranes is presented in Figure 2.

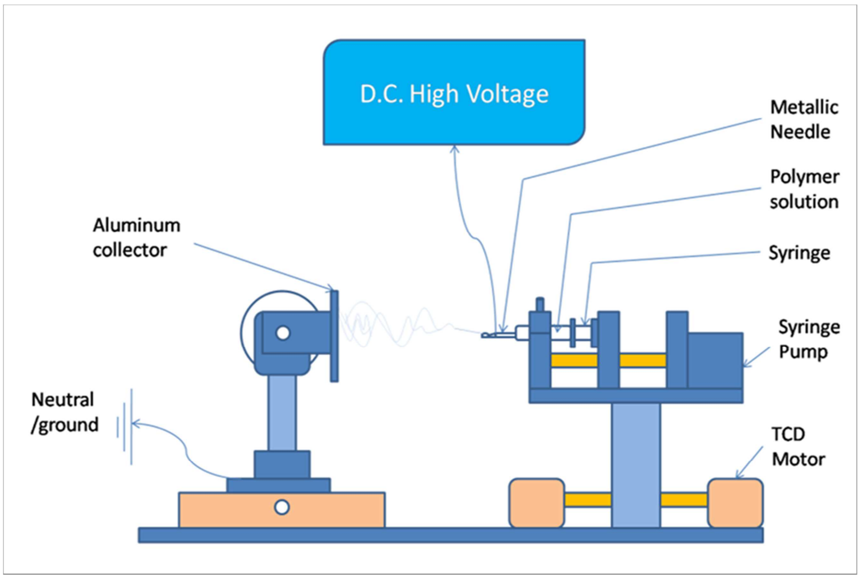

Figure 1. *Schematic diagram of the electrospinning setup.*

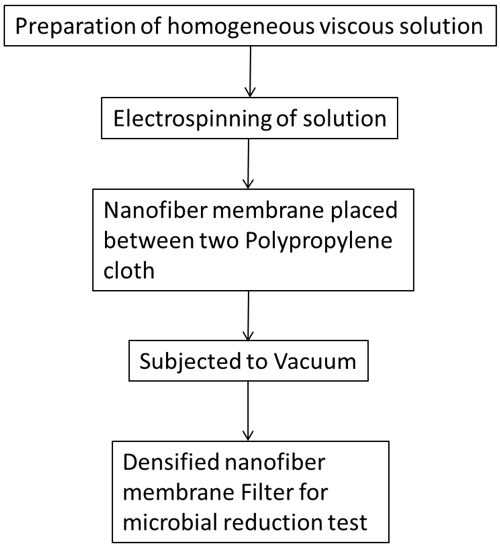

Figure 2. *Flow-sheet procedure to fabricate the electrospun nanofiber membrane filter.*

2.3. Characterization of Nanofibers

The morphological form of the electrospun fibers examined on Carl Zeiss EVO 18 scanning electron microscope. The diameter of the fibers was measured from the SEM images. Thickness of the as-electrospun nanofiber membrane and the filter membranes sandwiched between PP non-woven before and after subjecting to vacuum was also measured. The ATR FTIR spectra of the fiber membrane was recorded by keeping the membrane on the KBr crystal followed by scanning 125 times in the wave number range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} on Perkin Elmer Frontier MIR/FIR System. The DSC was carried out on PerkinElmer DSC-7 and presented in Figure 4 (b). About 3.5 mg of nanofiber sample was measured and kept in aluminum pan and lid arrangement. Sample is heated with a rate of 20°C/min in the range of 25°C to 350°C in nitrogen gas flowing at the rate of 10 ml/min.

2.4. Fabrication of NF Membrane Filter

The membrane filters were developed as follows. The electrospun membrane sample is placed between a pair of PP non-woven by lay-up for support and integrity. The sandwiched sample is inserted into the vacuum bag and sealed by mild heating. The bag is then transferred to a chamber where it was subjected to vacuum for a brief period of time. During this time, air inside and around the membrane is evacuated and the bag shrunk tightly around the sample reducing some of its thickness.

2.5. Microbial Reduction Test

The bacterial removal capabilities of filters were tested by membrane filtration method at M/s Eureka Forbes, Bengaluru, India. Briefly, 1 liter of *E. coli* MTCC 68 suspension (6.0×10^5 cfu/ml) at room temperature was passed through the sterile filter unit containing nanofiber membrane under gravity. The average flow rate was 20 ml/min. The number of viable bacteria after filtration was calculated using agar plate count method.

2.6. Water Flux Test

Membranes of different thickness for e.g. 125±13 µm, 250±25 µm, 500±50 µm, and 750±70 µm were electrospun to measure the effect of thickness on the flow rate (flux) of membranes. The membranes were cut in to a circular sample of diameter 8 cm (area, 50 cm^2) and put into a ceramic funnel for flux test. In-house prepared DI water was used for all flux measurements. Water was poured into the funnel to a height of 4 cm and maintained within ±0.2 cm by continuous pouring of water. This was repeated for 3 times (trial) for each of the membrane thickness. A graph of time taken to fill a 500ml cylinder Vs. trial numbers. From the above data, flux was also calculated as:

$$Flux\ = volume\ of\ water\ (\Delta v)/(Area\ of\ membrane * time\ for\ filling\ of\ \Delta v\ water \qquad (1)$$

3. Results and Discussion

3.1. Morphology of Nanofibers

The morphology and diameter of fiber is an important parameter that determines obtainable bacterial reduction value and water flux by the membrane. It is expected that membrane is made of ‘bead free' fibers of smallest diameters for greater microbial reduction from water. The SEM micrograph and corresponding diameter distribution of fibers electrospun from 10-16% (w/v) PAN/DMF solutions is shown in Figure 3. It can be observed from SEM micrographs that smooth fibers formed above 14%. Below 14% beads were observed due to poorer chain entanglement provided by lower viscosity of solution. With an increase in concentration, polymer chain could entangle to higher extent [6] resulting in bead disappearance. Therefore, 14% was used to prepare the membrane and presented in Figure 5. The diameter of electrospun nanofibers were in the range of 100 nm to 600 nm for the prepared 10-16% PAN in DMF solutions. The average fiber diameter was also observed to increase from 160 ± 43nm to 512 ± 76 nm with the increase in concentration of PAN solution from 10% to 16%. This is due to higher viscosity at higher concentrations. This trend is similar to observations already made in literature [6, 30]

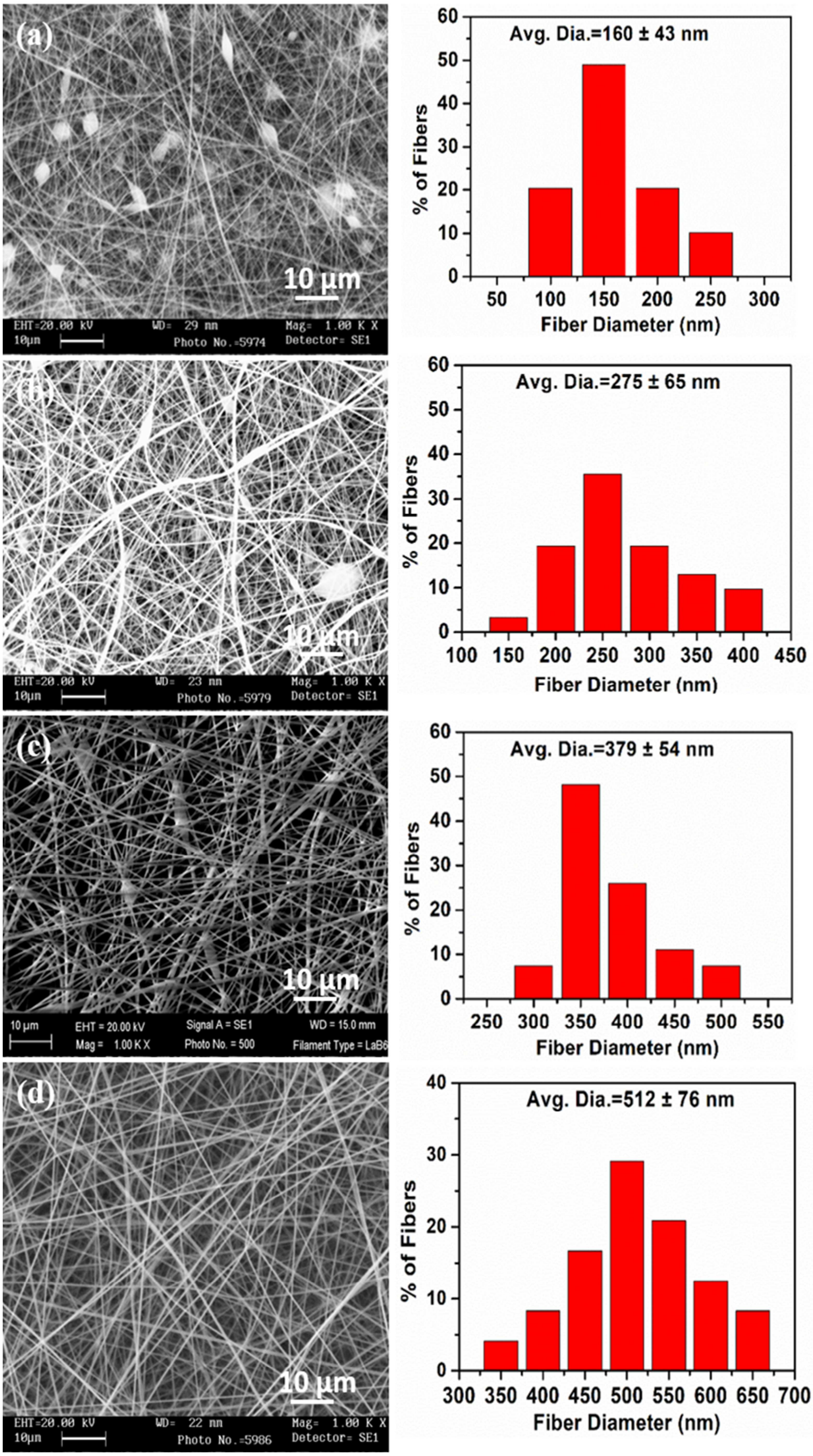

Figure 3. *SEM micrograph of PAN nanofibers and their diameter distribution at (A) 10% (A), (B) 12%, (C) 14%, (D) 16% of PAN in DMF solutions.*

3.2. FTIR and DSC of Nanofibers

The FTIR spectra of electrospun PAN nanofibers have been studied [29, 31]. Figure 4 (a) presents the ATR- FTIR spectrum of electrospun PAN nanofibers. The characteristic peaks of PAN are observed at 2937 cm^{-1} and at 2243 cm^{-1} are due to stretching vibrations of the methylene (CH_2) group and C≡N (nitrile) groups [29]. The peak at 1452 cm^{-1} is assigned to the bending vibration from the CH_2 group. The peak at 1690 cm^{-1} is assigned to the stretching of C=O of residual DMF. The observed peaks matched closely with the reported literature [29, 31].

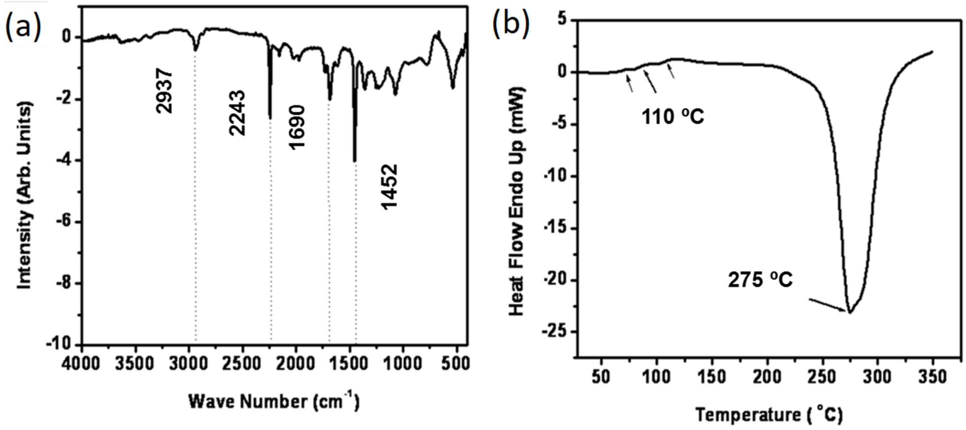

Figure 4. *FTIR spectra (A) and DSC thermogram (B) of electrospun PAN nanofiber membrane.*

Figure 4 (b) depicts the DSC endotherm of electrospun PAN nanofibers. The thermal transitions in PAN has been studied in the past and found the presence of multiple transitions in PAN [33]. S. Kenyon and M. J. Rayford studied dynamic mechanical properties and X- Ray Diffraction (X-RD) of cast PAN and molded PAN films and observed that PAN could have multiple glass transitions ($T_1>T_2>T_3$) due to existence of multiple phases and assigned the highest temperature transition for the main transition of the amorphous phase (T_1) and the secondary transition for amorphous phase (T_3) that is found lower than the transition for paracrystalline phase (T_2) [32]. In this work also, the PAN nanofibers showed three transitions (i) 101°C to 114°C (mid-point 107°C, T_1) (ii) 79°C - 90°C (mid-point 85°C, T_2) (iii) 64°C - 74°C (mid-point 69°C, T_3) similar to the literature [33]. In addition, the PAN fibers also exhibited a large exothermic transition in the temperature range of 250 - 350°C with a peak occurring at about 275°C. This is similar to observation made in the literature [26] and also compliments FTIR and TGA observations from T. J. Xue [34]. T. J. Xue et al. studied FTIR and TGA of pyrolysis products in the temperature range (250 - 310°C), observed the disappearance of nitrile stretching vibrations (2243 cm^{-1}) above 275°C and no weight loss until 287°C in TGA. This has been attributed cyclization and other exothermic reactions that are occurring during thermal degradation of PAN in the temperature range [34].

3.3. Bacteria Removal

Electrospun nanofiber membrane filter were tested by membrane filtration to determine the bacteria removal property tests were carried out to of nanofiber membrane. Figure 5 shows 14% PAN electrospun membrane used to prepare filter in this work. The thickness of this electrospun membrane was 3.5 ± 0.35 mm. The total thickness of filter including two PP cloth before subjecting to vacuum was 4.0 ± 0.35 mm. This thickness decreased to 3.3 ± 0.3 mm after application of the vacuum. This is about 17.5% reduction in the thickness of electrospun membrane after the vacuum application indicating partial densification. Considering thickness reduction in PP cloth is negligible, the observed thickness reduction is due to compaction of highly porous nanofiber membrane only. Reduction in porosity was indicated by reduced thickness. The bacterial reduction value for this filter membrane was 99.9997%. This value is close to reported value in the literature [3, 5]. The high value of bacterial reduction is due to (i) increased restriction for bacteria with increased thickness of the nanofiber membrane [6] and (ii) reduced pore size as well as pore volume after vacuum process.

Figure 5. *Photograph of electrospun PAN membrane.*

3.4. Flow Rate (Flux) Test

From figure 6, it is seen that time taken to fill 500 ml was lowest for 1st trial and then increases in subsequent trials. This is because a film of water sits on inner side of the pores due to its surface tension and viscosity, thereby, apparently reduces pore diameter. This apparent reduction in pore size requires more time to fill up 500 ml of water. The other reason could be the membrane becomes compact once water flows through it in first trial reducing the pore diameter.

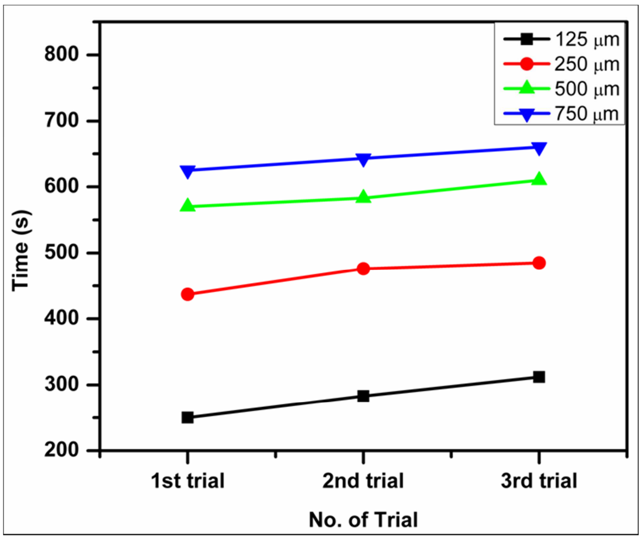

Figure 6. *Time taken to fill 500ml water Vs. trail numbers.*

From figure 7, it is seen that the flow rate decreases exponentially with the increase in membrane thickness. This is due to the strong resistance to flow through nanosized pores at higher thickness.

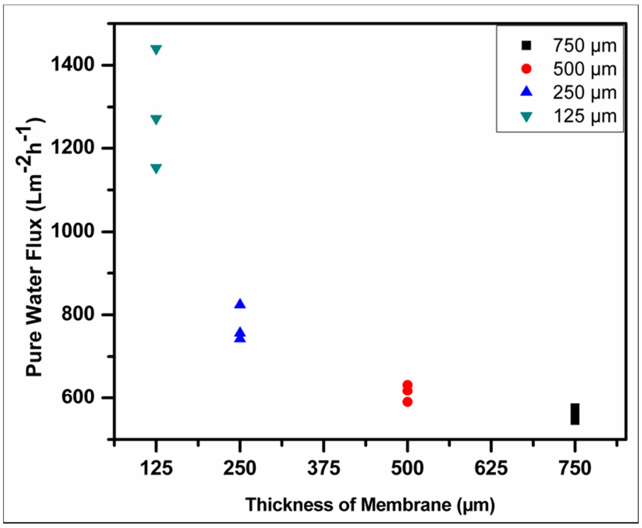

Figure 7. *Water flow rate (Flux) Vs. thickness of membrane.*

4. Conclusions

In this paper, PAN nanofibers of diameters in the range of 50 to 750 nm were prepared by varying solution concentration in the range of 10 to 16% (w/v). SEM micrographs indicated that bead-free fibers were obtained at 14% with average diameter of 379 ± 54 nm.

The DSC study revealed presence of three glass transition temperatures: a main transition of the amorphous phase at 107°C (T_1); a paracrystalline phase transition at 85°C (T_2) and a secondary transition for amorphous phase at 69°C (T_3). FTIR study confirmed the nitrile and methyl groups present in PAN.

Filters were prepared by sandwiching electrospun nanofiber membranes between two polypropylene cloths and subjecting to vacuum. Membrane filtration tests on the filters indicated 99.9997% *E. coli* bacteria elimination at thickness of about 3.3 ± 0.35 mm after vacuum process. The developed filters may find use for bacterial removal from drinking water for home use.

Acknowledgements

The authors would like to acknowledge Water Technology Initiative (WTI), Dept. of Science and Technology (DST), New Delhi, India for sanctioning a project (sanction order no. DST/TM/WTI/2K14/205/(G)). The authors are thankful for Ms. Kalavati, Mr. Srinivasa and Mr. Krishna for their help in taking SEM images, FTIR and DSC scans respectively. The authors are thankful to M/s Eureka forbes for carrying out bacterial reduction test.

References

[1] R. Gopal, S. Kaur, C. Y. Feng, C. Chan, S. Ramakrishna, S. Tabe, and T. Matsuura, Electrospun nanofibrous polysulfone membranes as pre-filters: Particulate removal, *J. Membr. Sci.*, 289, 210 (2007).

[2] M. Faccin, G. Borja, M. Boerrigter, D. M. Martín, S. M. Crespiera, S. Vázquez-Campos, L. Aubouy, and D. Amantia, Electrospun carbon nanofiber membranes for filtration of nanoparticles from water, *J. Nanomater.*, 2 (2015).

[3] A. Sato, R. Wang, H. Ma, B. S. Hsiao, and B. Chu, Novel nanofibrous scaffolds for water filtration with bacteria and virus removal capability, *J. Electron Microsc.*, 60, 201 (2011).

[4] H. Ma, B. S. Hsiao, and B. Chu, Electrospun nanofibrous membranes for high flux microfiltration, *J. Membr. Sci.*, 60, 446 (2014).

[5] H. Ma, C. Burger, B. S. Hsiao, and B. Chu, Ultra-fine cellulose nanofibers: new nano-scale materials for water purification, *J. Mater. Chem.*, 21, 7507 (2011).

[6] R. Wang, Y. Liu, B. Li, Hsiao BS, and Chu B. Electrospun nanofibrous membranes for high flux microfiltration, *J. Membr. Sci.*, 392, 167 (2012).

[7] K. Saeed, S. Haider, T. J. Oh, and S. Y. Park, Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption, *J. Membr. Sci.*, 322, 400 (2008).

[8] S. Patel, and G. Hota, Adsorptive removal of malachite green dye by functionalized electrospun PAN nanofibers membrane, *Fibers Polym.*, 15, 2272 (2014).

[9] R. Zhao, Y. Wang, X. Li, B. Sun, Y. Li, H. Ji, J. Qiu, and C. Wang, Surface activated hydrothermal carbon-coated electrospun PAN fiber membrane with enhanced adsorption properties for herbicide, *ACS Sustainable Chem. Eng.*, 4, 2584 (2016).

[10] M. Jambrich, and P. Hodul, Textile applications of polypropylene fibers, in *Polypropylene*, Springer, Dordrecht, (1999).

[11] P. Biswas, and R. Bandyopadhyaya, Water disinfection using silver nanoparticle impregnated activated carbon: Escherichia coli cell-killing in batch and continuous packed column operation over a long duration, *Water Res.*, 100, 105 (2016).

[12] E. A. Garcia, M. A. Barcelo, P. Bond, J. Keller, W Gernjak, and J. Radjenovic, Hybrid electrochemical-granular activated carbon system for the treatment of greywater, *Chem. Eng. J.*, 352, 405 (2018).

[13] J. Radjenovic, M. Petrovic, F. Ventura, and D. Barcelo, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, *Water Res.*, 42, 3601 (2008).

[14] W. A. Hijnen, E. F. Beerendonk, and G. J. Medema, Inactivation credit of UV radiation for viruses, bacteria and protozoan cysts in water: a review, *Water Res.*, 40, 3 (2006).

[15] S. Ramakrishna, K. Fujihara, W. E. Teo, T. Yong, Z. Ma, and R. Ramaseshan, Electrospun nanofibers: solving global issues, *Mater. Today*, 9, 40 (2006).

[16] L. Persano, A. Camposeo, C. Tekmen, and D. Pisignano, Industrial upscaling of electrospinning and applications of polymer nanofibers: a review, *Macromol. Mater. Eng.*, 298, 504 (2013).

[17] P. K. Panda, and B. Sahoo, Synthesis and Applications of Electrospun Nanofibers - A Review, In: *Nanotechnology Vol. 1: Fundamentals and Applications*, Stadium Press, New Delhi, 399 (2013).

[18] P. K. Panda, Ceramic nanofibers by electrospinning technique—A review, *Trans. Ind. Ceram. Soc.*, 66, 65 (2007).

[19] D. W. Hutmacher, and P. D. Dalton, Melt electrospinning, *Chem. - Asian J.*, 6, 44 (2011).

[20] S. Sundarrajan, K. L. Tan, S. H. Lim, and S. Ramakrishna, Electrospun nanofibers for air filtration applications, *Procedia Eng.*, 75, 159 (2014).

[21] A. Eatemadi, H. Daraee, N. Zarghami, M. H. Yar, and A. Akbarzadeh, Nanofiber: synthesis and biomedical applications, *Artif. Cells, Nanomed. Biotechnol.*, 44, 111 (2016).

[22] S. F. Chou, D. Carson, and K. A. Woodrow, Current strategies for sustaining drug release from electrospun nanofibers, *J. Control. Release,* 220, 584 (2015).

[23] J. Sheng, Y. Xu, J. Yu, and B. Ding, Robust fluorine-free superhydrophobic amino-silicone oil/SiO_2 modification of electrospun polyacrylonitrile membranes for waterproof-breathable application, *ACS Appl. Mater. Interfaces*, 9, 15139 (2017).

[24] A. Raza, Y. Li, J. Sheng, J. Yu, and B. Ding, Protective clothing based on electrospun nanofibrous membranes, in *Electrospun Nanofibers for Energy and Environmental Applications,* Springer, Berlin (2014).

[25] D. Chen, T. Liu, X. Zhou, W. C. Tjiu, and H. Hou, Electrospinning fabrication of high strength and toughness polyimide nanofiber membranes containing multiwalled carbon nanotubes, *J. Phys. Chem. B*, 113, 9741 (2009).

[26] M. Botes, and C. T. Eugene, The potential of nanofibers and nanobiocides in water purification, *Crit. Rev. Microbiol.,* 36, 68 (2010).

[27] G. S. Simate, S. E. Iyuke, S. Ndlovu, M. Heydenrych, and L. F. Walubita, Human health effects of residual carbon nanotubes and traditional water treatment chemicals in drinking water, *Environ. Int.* 39, 38 (2012).

[28] J. Lee, J. Yoon, J. H. Kim, T. Lee, and H. Byun, Electrospun PAN–GO composite nanofibers as water purification membranes, *J. Appl. Polym. Sci.*, 135, 45858 (2018).

[29] Y. Aykut, B. Pourdeyhimi, and S. A. Khan, Effects of surfactants on the microstructures of electrospun polyacrylonitrile nanofibers and their carbonized analogs, *J. Appl. Polym. Sci.*, 130, 3726 (2013).

[30] R. Sandhya, and P. K. Panda, Effect of polymer concentration on morphology of polyacrylonitrile (PAN) nanofibers prepared by electrospinning technique, *Nano Sci. Nano Technol.: Indian J.*, 7, 125 (2013).

[31] D. G. Yu, N. P. Chatterton, J. H. Yang, X. Wang, and Y. Z. Liao, Coaxial Electrospinning with Triton X‑100 Solutions as Sheath Fluids for Preparing PAN Nanofibers, *Macromol. Mater. Eng.*, 297, 395 (2012).

[32] A. S. Kenyon, and M. J. Rayford, Mechanical Relaxation Processes in Polyacrylonitrile Polymers and Copolymers, *J. Appl. Polym. Sci.*, 23, 717 (1979).

[33] L. Ji, A. J. Medford, and X. Zhang, Electrospun polyacrylonitrile/zinc chloride composite nanofibers and their response to hydrogen sulfide, *Polymer,* 50, 605 (2009).

[34] T. J. Xue, M. A McKinney, and C. A. Wilkie, The thermal degradation of polyacrylonitrile, *Polym. Degrad. Stab.*, 58, 193 (1997).