

Electrospinning of Nanofibrous Membrane

Subjects: Polymer Science

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Among the different fabrication approaches of nanofibrous membrane, electrospinning is considered as the most favorable and effective due to its advantages of controllable process, high production efficiency, and low cost.

Keywords: electrospinning ; nanofibrous membrane ; air filtration

1. Introduction

For the material of air filtration membrane, nanofiber has gained increasing interest from researchers due to its wide applications in various disciplines such as filter medium, tissue engineering scaffolds, composite materials, artificial blood vessels, biochips, drug delivery, nanosensors, optics, etc., Moreover, its unique advantages of large specific surface area and ultra-fine porosity make it a promising candidate for air filtration membrane material. Because of these effects, the chemical and physical properties of nanofiber are changed. Characteristics of electrospun nanofibrous membranes, such as low Knudsen number, ^[1] slip flow effect causing the decrease of pressure drop, ^[2] and the formation of garland leading to better filtration efficiency, ^[3] etc.

(a) Schematic diagram of processing steps for the fabrication of nanofibers. (b) Main filtration mechanism of air filter. Elsevier B.V. (c) Schematics showing the fabrication of transparent air filter by electrospinning.

As a well-explored research field of nanotechnology, there are already many reviews covering electrospinning techniques and various applications of nanofibrous membranes, including reviews by Robert et al. Because of the swift development of electrospinning techniques, the research topic of electrospun membranes as air filtration medium is gaining focus. Despite these previous works, our review, covering mainly the latest progress and contributions, serves as a renewal for this topic, provides summarization and comparison of novel electrospinning techniques, electrospinning products with their new applications, and our views on future trends and perspectives. In this review, we provide an overview of electrospinning techniques, along with structures of electrospun air filtration membranes, then, functions and characteristics of filtration membranes are summarized, and finally, we focus on some applications of electrospun nanofiber air filtration membranes.

2. Electrospinning Techniques

Electrospinning machines mainly consist of high-voltage DC power supplies, injection pumps, spinning nozzles, and collecting devices. The process of fabricating nanofibers is: a metal wire connects the needle to the positive electrode of the high-voltage generator. It may also be a metal surface or other collecting device such as a rotary drum to meet the conditions of different experiments. Under a powerful electric field force, the polymer solution or melt (generally non-Newtonian fluid) overcomes its surface tension and viscoelastic force to generate charge, the mutual exclusion between charges, and the opposite charge electrode's compression to the surface charge, directly creating a force that is opposite to the surface tension.

Divided by the state of the polymer used to fabricate nanofiber membranes, electrospinning can be categorized into solution electrospinning and melt electrospinning ^[4], the latter is also known as solvent-free electrospinning ^[5]. The most conventional and most widely used solution electrospinning, or single nozzle electrospinning, is relatively simple to set up and operate, but the low production rate and residue of organic/toxic solvent in nanofibers remain as the major challenges. The leading research progress of needleless electrospinning and multi-needle electrospinning shows a trend of fast and up-scaling production of electrospinning membranes, which solidifies the foundation of their expanded applications in air filtration. Melt electrospinning reduces the usage of toxic solvents, thus it is considered as more environmentally friendly than solvent electrospinning.

Due to the absence of needle-like spinnerets, needleless electrospinning is immune to the common problem of clogging and low productivity faced by single needle electrospinning. [6] reported the fabrication of ultrafine polyamide 6 (PA-6) nanofiber membranes via needleless electrospinning process, during which the relative humidity condition and electrode type were both controlled. Compared with needle electrospinning, this wire loop spinneret generates a stronger electric field, and the production rate of nanofiber membranes was 0.48 g·h⁻¹. According to the advanced research mentioned above, it is apparent that needleless electrospinning is a promising way to lift the production rate of nanofiber membranes, compared with its needle electrospinning rival.

The mechanism of multi-needle electrospinning is similar to the conventional single needle electrospinning, and like needleless electrospinning, multi-needle electrospinning system usually includes a specially designed spinneret with a unique structure, which contains several nozzles working simultaneously. To tackle the problem of nonuniform electric field of the needle tip caused by the overly intensive arrangement of needles, Zhu et al. With the introduction of sheath gas, the resultant productivity reached 0.618–0.712 g·h⁻¹, which was 30–50 times as that of the conventional electrospinning. Multi-needle electrospinning exhibits even better production rate than the needleless electrospinning, making the scale-up of nanofiber membranes fabrication possible.

Polymer is directly heated for the formation of fibers in melt electrospinning and the produced fibers have fewer defects and better mechanical properties besides higher yield [7]. Five polyamide and polyolefin-based polymers were tested, and a wide range of fiber morphologies and high dispersion of fiber diameter were observed. [8] produced poly(ether-block-amide)(PEBA) fibers by melt electrospinning, and studied the effect of parameters on fiber diameter. At the highest and lowest drum speed, align fiber and crosslinking fiber were formed respectively.

Compared with the most common single needle electrospinning, other electrospinning techniques mentioned in this chapter, including needleless, multi-needle, and solvent-free electrospinning, have unique merits suitable for different fabrication demands, and drawbacks that need to be considered. The relatively easy maintenance of needleless electrospinning set-up is another advantage, which can save the time and finance cost in the production process. Unlike needleless electrospinning, there is less evaporation during the multi-needle electrospinning process, which results in the higher production rate than needleless electrospinning. Similar to the needleless electrospinning, without the application of nozzles, the control difficulty still exists in melt electrospinning.

3. Applications in Air Filtration

Electrospun polymer membranes have already been proved highly effective against PM2.5 pollution. The unique features of high filtration efficiency and low pressure drop together guarantee the extensive application in the field of air filtration of PM2.5. The filtration performance is further enhanced by the development of electrospinning process, structures, and materials, making the electrospun membranes highly adaptable in individual protection both outdoor and indoor.

The application of outdoor protection is concentrated on high-efficiency filtration masks. In addition to high filtration efficiency, low pressure drop is another key factor which is decisive to the actual usage of electrospun membranes, because as a piece of protective garment, masks should exhibit good air permeability and breathability. Moreover, these masks provide protection for individuals even in harsh conditions owing to their special advantages such as high porosity, high mechanical strength, and multi-functions like thermostability, antibacterial activity.

Compared with commercial masks, this air filtration mat exhibited higher filtration efficiency under thick haze. The fabricated NFM1.5 mask displayed high filtration efficiency of 99.99%, low pressure drop of 67 Pa, and low basis weight of 4.32 g/m². More importantly, due to its ultralight basis weight and high porosity, NFM1.5 mask had a distinct radiative cooling effect, which guaranteed the wearing comfort while providing better protection than commercial face masks. [9] fabricated nanofibrous protective masks from PAN and MC by electrospinning, and these masks displayed strong antimicrobial efficacies against both *S. aureus* and *E. coli* O157:HH7.

Application of electrospun multifunctional nanofibrous filtration masks, serving as an effective physical protection, is a key strategy to prevent viral infection [10]. During the electrospinning process, vinyl alcohol and PVA/SAP were simultaneously coated onto face masks, resulting in their virus protection and comfort properties. In addition to electrospun masks, antimicrobial materials could be made into protective clothing, which had potential in providing extra and extensive protection. [11] developed a roll-to-roll method to fabricate masks based on fast transfer of electrospun nanofiber film from roughed metal foil to a receiving mesh substrate.

Photographs of the mask preparation process with 05GOPAN membrane as a wearable air filter. Photographs and SEM images (insets) showing the filter effect of 05GOPAN membrane after filtration of different times. Elsevier B.V. (b) Thermal images of bare face and faces covered with NMF1.5 and two commercial face masks. Elsevier Inc. (d) Schematic

representation of the design of the nanofibrous respirator face mask; (i) depicts the respirator filter containing multilayers of CuONPs/GO@PLA and CuONPs/GO@CA nanofibers.

The indoor air quality, as one of the most important living conditions, is of residents' concern because like outdoor PM pollution, the indoor air pollution is also a threat to public health because of the long time of exposure. Unlike the outdoor application of filtration masks, which are mostly worn outside, the indoor air filtration mainly relies on air filters to screen the PM off the household or other indoor settings. There are already several air filters in service [12], but the novel electrospun nanofiber membranes with exceptional filtration efficiency can easily outperform their commercial rivals.

As for the advanced electrospun filters, Han et al. [13] reported an electrically activated ultrathin PVDF-TrFE nanofiber air filter with high PM1.0 filtration efficiency of 94%. This nanofiber filter also exhibited good light transmittance of 65%, which allows it to be installed on the window frames of houses as an economically affordable way to prevent indoor air pollution instead of applying expensive air circulation systems (Figure 13a). [14] produced composite electrospun membrane electret filter using PAN and SiO₂NPs between nonwoven fabrics, and the fabricated membrane with SiO₂ showed better filtration performance than commercial filter medium.

Another source of PM that possibly exists in the household is the industrial dust emitted from 3D printing, as 3D printers are becoming increasingly accessible. [15] expanded the application scenarios of electrospun filters to industrial emissions like 3D printing. The electrospinning process was optimized using design of experiment (DOE), and bead-free PAN nanofibers with diameter of <100 nm was formed. The fabricated membranes were used to filter PM_{2.5} emissions from FDM 3D printing and the PAN membrane with diameter of 77 nm showed a filtration efficiency of 81.16% (Figure 1).

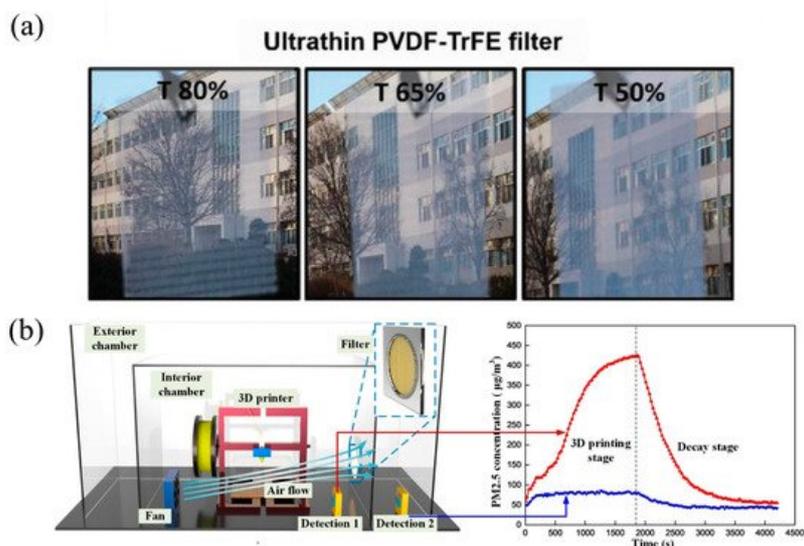


Figure 1. (a) Photographs of the PVDF-TrFE nanofiber filters with different light transmittances (T): 80%, 65%, and 50%. Adapted with permission from ref. (b) Schematic of particles filtration experiment during 3D printing. Reprinted with permission from ref.

The most common applications of electrospun filtration membranes can be roughly concluded as outdoor protection and indoor protection, namely filtration masks and indoor air filters. As a wearable protection against air pollution, the application of filtration masks shows a trend toward good wearing comfort, extra functions that can offer protection even in harsh conditions, while the indoor air filters, which often serve as guards around the household, demand good transmittance, high durability, and low cost.

Despite the above eye-catching progress, there are still problems and challenges to be solved and tackled in the future for these electrospun membranes to become off-the-shelf productions. To solve this problem, the spectrum of electrospinning materials needs to be enlarged. Green and biodegradable materials introduced in Section 4.4 are ideal candidates for the environment-friendly disposal of these nanofibrous masks and filters. Furthermore, research on electrospinning using recycled materials needs to be done, as domestic plastic waste can be a promising source for the recycled polymers [16].

References

1. Shou, D.; Ye, L.; Fan, J. Gas transport properties of electrospun polymer nanofibers. *Polymer* 2014, 55, 3149–3155.

2. Bao, L.; Seki, K.; Niinuma, H.; Otani, Y.; Balgis, R.; Ogi, T.; Gradon, L.; Okuyama, K. Verification of slip flow in nanofiber filter media through pressure drop measurement at low-pressure conditions. *Sep. Purif. Technol.* 2016, 159, 100–107.
3. Xin, Y.; Reneker, D.H. Garland formation process in electrospinning. *Polymer* 2012, 53, 3629–3635.
4. Lian, H.; Meng, Z. Melt electrospinning vs. solution electrospinning: A comparative study of drug-loaded poly (ϵ -caprolactone) fibres. *Mater. Sci. Eng. C* 2017, 74, 117–123.
5. Muerza-Cascante, M.L.; Haylock, D.; Hutmacher, D.W.; Dalton, P.D. Melt electrospinning and its technologization in tissue engineering. *Tissue Eng.—Part B Rev.* 2015, 21, 187–202.
6. Yan, S.; Yu, Y.; Ma, R.; Fang, J. The formation of ultrafine polyamide 6 nanofiber membranes with needleless electrospinning for air filtration. *Polym. Adv. Technol.* 2019, 30, 1635–1643.
7. Morikawa, K.; Green, M.; Naraghi, M. A Novel Approach for Melt Electrospinning of Polymer Fibers. *Procedia Manuf.* 2018, 26, 205–208.
8. Sarwar, Z.; Krugly, E.; Danilovas, P.P.; Ciuzas, D.; Kauneliene, V.; Martuzevicius, D. Fabrication and characterization of PEBA fibers by melt and solution electrospinning. *J. Mater. Res. Technol.* 2019, 8, 6074–6085.
9. Huang, C.; Liu, Y.; Li, Z.; Li, R.; Ren, X.; Huang, T.S. N-halamine antibacterial nanofibrous mats based on polyacrylonitrile and N-halamine for protective face masks. *J. Eng. Fiber. Fabr.* 2019, 14, 1558925019843222.
10. Tang, Z.; Kong, N.; Zhang, X.; Liu, Y.; Hu, P.; Mou, S.; Liljeström, P.; Shi, J.; Tan, W.; Kim, J.S.; et al. A materials-science perspective on tackling COVID-19. *Nat. Rev. Mater.* 2020, 5, 847–860.
11. Xu, J.; Liu, C.; Hsu, P.C.; Liu, K.; Zhang, R.; Liu, Y.; Cui, Y. Roll-to-Roll Transfer of Electrospun Nanofiber Film for High-Efficiency Transparent Air Filter. *Nano Lett.* 2016, 16, 1270–1275.
12. Cai, R.R.; Zhang, L.Z.; Yu, C.W. Advanced electrospun filters to protect building environments from pollution. *Indoor Built Environ.* 2019, 28, 147–151.
13. Han, K.S.; Lee, S.; Kim, M.; Park, P.; Lee, M.H.; Nah, J. Electrically Activated Ultrathin PVDF-TrFE Air Filter for High-Efficiency PM1.0 Filtration. *Adv. Funct. Mater.* 2019, 29, 1–7.
14. Gobi, N.; Vijayalakshmi, E.; Robert, B.; Srinivasan, N.R. Development of PAN nano fibrous filter hybridized by SiO₂ nanoparticles electret for high efficiency air filtration. *J. Polym. Mater.* 2019, 35, 317–328.
15. Cao, M.; Gu, F.; Rao, C.; Fu, J.; Zhao, P. Improving the electrospinning process of fabricating nanofibrous membranes to filter PM2.5. *Sci. Total. Environ.* 2019, 666, 1011–1021.
16. Šišková, A.O.; Frajová, J.; Nosko, M. Recycling of poly(ethylene terephthalate) by electrospinning to enhanced the filtration efficiency. *Mater. Lett.* 2020, 278, 2–4.