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Photo-crosslinked PVA/PEI electrospun nanofiber membranes: Preparation and preliminary evaluation in virus clearance tests

Bihter Zeytuncu[a,d,1,*], Melike Ürper[b,c], İsmail Koyuncu[b,c], Volodymyr V. Tarabara[d,**]

[a] Applied Research Center of Materials Science and Production Technology, Istanbul Technical University, Istanbul 34469, Turkey
[b] National Research Center on Membrane Technologies (MEM-TEK), Istanbul Technical University, Maslak, Istanbul 34469, Turkey
[c] Environmental Engineering Department, Faculty of Civil Engineering, Istanbul Technical University, Maslak, Istanbul 34469, Turkey
[d] Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824, USA

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ABSTRACT

We report on the preparation of electropositive nanofiber membranes by electrospinning with in situ photo-crosslinking and their preliminary evaluation in virus adsorption and removal tests. Poly(vinyl alcohol) (PVA) and polyethyleneimine (PEI) were modified with glycidyl methacrylate, to form an acrylated crosslinked polymer (a-PVA/a-PEI) upon UV exposure during the electrospinning process. The a-PVA/a-PEI nanofibers were electrospun on a non-woven polyester support to form an electropositive ($\zeta = 7$ mV at pH 7.4) and hydrophilic ($\theta_w \sim 53^\circ$) membrane with the mean pore size of 0.48 μm. The microfilter had the specific permeate flux of $\sim 6.9 \cdot 10^4$ L/(m^2·h·bar), comparable with that of commercially available membranes of similar nominal pore sizes. Adsorption of the negatively charged and hydrophilic bacteriophage MS2 ($d \sim 27$ nm) onto the membrane followed Freundlich isotherm and could be classified as favorable with the average adsorption intensity $n^{-1} \sim 0.91$. The 99% retention of MS2 in flow-through virus clearance tests was attributed to adsorption and was likely controlled by the limited detention time within the membrane.

1. Introduction

Electrospinning is commonly used to make nanofibers ranging from ~10 nm to several hundred nanometers in diameter [1]. Comparatively simple and inexpensive [2,3], the electrospinning method offers an alternative to other nanofiber manufacturing techniques such as drawing, template synthesis, phase separation and self-assembly [4]. Electrospinning relies on electrostatic forces to draw ultrafine solid threads from solutions of polymers of sufficiently high molecular weight and does not require coagulation chemistry or high temperatures [1,5]. Fiber mats produced by electrospinning are lightweight and characterized by high porosity, small inter-fiber pore size and large surface area [1,6]. Electrospun nanofiber membranes (ENMs) have found a wide range of applications including drug delivery [7], scaffolding in tissue engineering [8], clothing protection [9], sensing [10], as well as adsorption [11,12] and filtration [13]. In membrane filtration applications, ENMs have been used as microfilters [14,15] and as supporting layers for both ultrafilters and salt-rejecting membranes [16]. The high porosity and interconnected pore structure of ENMs brings about increased permeability and higher separation throughput.

Many polymers processable by electrospinning are water-soluble and, when unmodified, are not suitable as materials for water treatment membranes [17,18]. Physical or chemical crosslinking of polymer structures is a common method of rendering the nanofibers insoluble and increasing their thermal and chemical stability. Most ENMs have been produced by post-spinning crosslinking, as well as pre-crosslinking. Each of these approaches, however, adds another step to the fabrication process. Furthermore, pre-crosslinking, which involves mixing the polymer solution and chemical crosslinker, could lead to gel formation making continuous or large scale production difficult [19]. In our previous study, in situ UV radiation was implemented *during* electrospinning to achieve crosslinking [12,20,21]. In addition to being a fast one-step process, this novel approach can ensure high crosslinking efficiency to minimize the amount of unreacted and leachable cytotoxic agents.

Key metrics of ENMs are fiber morphology and surface chemistry. The former defines the nominal pore size and the permeability of the fiber mat while the latter governs adsorptive characteristics of the material. ENMs can be used to remove microorganisms from water either in purification applications or for pathogen detection. For example,

* Corresponding author at: Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824, USA.
** Corresponding author.
E-mail addresses: bihterzeytuncu@gmail.com (B. Zeytuncu), tarabara@msu.edu (V.V. Tarabara).
[1] Present address: National Research Center on Membrane Technologies (MEM-TEK), Istanbul Technical University, Maslak, Istanbul 34469, Turkey.

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VIRADEL (VIRus ADsorption and ELution) method employs charged microporous filters to concentrate viruses from water samples for further detection by downstream assays [22]. Viruses, with their size typically in the 20 to 200 nm range are too small for size exclusion by microfilters to be effective [15]. Instead, electrostatic interactions between the filter surface and viruses are employed to ensure sufficient removal. Because the charge of most viruses at pH typical for natural aqueous media is negative, electropositive filters are a common choice. The attractive feature of electropositive filtration is that virus removal can be achieved even though the pore size is much larger that the virus; the large pore size and porosity enable high permeate fluxes making high throughput separations possible [23].

Significant amount of work has been done on virus adsorption by free nanofibers (i.e. nanofibers not cast as a membrane) – both electrospun and otherwise. For example, Mi et al. demonstrated that crosslinked N-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan (HTCC) – polyvinyl alcohol (PVA) nanofibers adsorbed enveloped and nonenveloped viruses [24]; although ENMs were produced in this study, their separation properties (e.g. water permeability and nominal pore size) were not evaluated. Bai et al. showed that functionalization of electrospun chitosan nanofibers by a quaternary amine increased porcine parvovirus (< 25 nm) removal from 30% to 70% [25]. Park and Kim prepared PVA nanofibers containing a quaternary ammonium compound (benzyl triethylammonium chloride) as an antimicrobial agent and showed that, in addition to bacteria, bacteriophages MS2 and PhiX174 could be removed; the removal was attributed to hydrophobic interactions between quaternary ammonium and viruses although the mechanism of inactivation remained unclear [26].

While virus adsorption to free nanofibers has been explored extensively, to our knowledge, only three studies to date have evaluated ENMs for their ability to remove viruses from water. Working with bacteriophage MS2, Chu and colleagues first reported 99.99% retention of MS2 by composite fibrous membranes modified with PEI [27]. Wang et al. showed that two-layered polyacrylonitrile (PAN)/polyethyleneterephthalate (PET) ENMs amended with ultrafine (~5 nm) cellulose nanofibers achieved 99.99% removal for MS2 [28]. The same degree of removal of this bacteriophage was achieved in another study where by Ma et al. used poly(1-(1-vinylimidazolium) ethyl-3-vinylimdazoliumdibromide/PAN ENMs and attributed the high removal of the virus to its adsorption to the membrane [29].

The goal of the present work was to evaluate the feasibility of electrospinning with in situ crosslinking as a one-step method of fabricating electropositive water-stable membranes with high capacity for virus adsorption. We designed such membranes using PVA and PEI as base polymers. A biodegradable hydrophilic polymer, PVA is easy to process and functionalize and has high chemical and thermal resistance [12,20]. The hydrophilicity of PVA should help make the resulting membrane more resistant to fouling. PVA is also a highly versatile material whose properties can be adjusted by regulating the degree of hydrolysis [30]. PEI is an aliphatic polyamine containing primary, secondary, and tertiary amines, which make this polymer suitable for producing polycationic nanofibers [19]. PEI is water-soluble and, unmodified, cannot be used as a material for water treatment membranes [17,18]; thus to fabricate water-stable ENMs, PVA and PEI where photo-crosslinked during electrospinning. We characterized ENMs in terms of their morphological, chemical, and hydraulic properties and evaluated the filters in virus removal tests.

2. Materials and methods

2.1. Materials

Poly(vinyl alcohol) (PVA; 87–89% hydrolyzed, 146–186 kDa), glycidyl methacrylate (GMA; 97%) and tetraethylmethylenediamine (TEMED) were purchased from Sigma Aldrich. Polyethyleneimine (PEI; 60 kDa) was obtained from Alfa Aesar. The radical photoinitiator, 2-hydroxy-2-methyl-1-phenyl-1-propan-1-one (Darocur 1173) was supplied by Ciba Specialty Chemicals. Dimethyl sulfoxide (DMSO), chloroform and ethylene alcohol were purchased from Merck. All chemicals were used as received from vendors without further purification. The polyester (polyethyleneterephthalate (PET); CraneMat® CU 434 UF nonwoven fabric sheets (porosity of 181 L/m^2/s at 200 Pa) used as support materials were supplied by Neenah Technical Materials.

2.2. Preparation of membrane casting solutions

Prior to the preparation of membrane casting solutions, PVA and PEI were acrylated with GMA to enable photopolymerization during the electrospinning process. First, PVA was reacted with GMA following the procedure described by Crispim et al. [31]. Briefly, PVA was dissolved in DMSO at ~70 °C to yield 80 g(PVA)/L. GMA was then added dropwise into the solution magnetically stirred in the presence of TEMED as a catalyst at 70 °C for 4 h. The acrylated PVA (a-PVA) was precipitated three times using ethanol as a non-solvent and then dried under vacuum for 1 week. Second, GMA was added drop by drop to a PEI solution in 10 mL of chloroform at 0 °C to prepare acrylated PEI (a-PEI) and the solution was vigorously stirred overnight at room temperature in an flask wrapped in aluminum foil [19]. In the GMA/PEI mixture, the molar ratio of the secondary amine group on PEI to the epoxy group on GMA was 1.69:1. Then the acrylated PEI was precipitated with acetone to remove free GMA. The residue was washed with acetone three times and then filtered, dried, and stored in the fridge. Scheme 1 shows reaction pathways for the synthesis of a-PVA and a-PEI. The membrane casting solution was prepared by dissolving 5 g a-PVA and 1 g a-PEI (i.e. PVA:PEI mass ratio of 5:1) in 5 mL of ethanol with 3 wt% admix of Darocur 1173.

2.3. Synthesis of electrospun nanofiber membranes

The prepared solution was placed in a syringe connected to the positive terminal of a high-voltage (20 kV) power supply. The negative terminal of the power supply unit was connected to a conductive collector positioned 15 cm away from the syringe needle. The solution was spun at the flow rate of 0.10 mL/h for 10 h at room temperature while being irradiated by UV light (λ_{max} = 365 nm, OSRAM 300 W high pressure UV lamp). The fibers were collected on the PET filter support paper (Fig. 1). The non-woven PET support helped improve the mechanical stability of the membranes as unsupported ENMs are fragile.

To improve mechanical properties of ENMs they were subjected to compression and heat treatment [24]. Square (50 mm × 50 mm) pieces of the cast ENM mats were cut, layered and placed in between two 100 mm × 100 mm square dies. For each membrane, 4 layers were compressed by a manual hydraulic press (Specac) at a load of 5 MPa for 1 min [32]. Then the ENM sheets were placed into a preheated oven at 90 °C for 10 min.

2.4. Membrane characterization

The infrared absorption spectra of the prepared ENMs were recorded using an FTIR spectrometer (Nicolet 6700). The morphology of ENMs was assessed using the ultra-high resolution scanning electron microscope (SEM; JEOL 7500F). The pore size of ENMs was measured by capillary flow porometer (Quantachrome 3GWin). Membrane porosity, ε, was determined gravimetrically as follows: first the volume of electrospun membrane (V_{tot}) was calculated by multiplying the thickness of the membrane by its surface area. Second, the mass of water was converted to the pore volume, V_{pore}, of the membrane in the assumption that all pores were filled with water. Finally, the pore volume was divided by the total volume to give membrane porosity: $\varepsilon = \frac{V_{pore}}{V_{tot}} \times 100\%$. The ζ-potential of ENMs was measured using Anton Paar Surpaas electrokinetic analyzer. The water contact angle on ENM surface was