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Influence of the amount of poly(vinyl alcohol) on the *in situ* production of photo-crosslinked thioamide functionalized nanofiber membranes

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Abstract: Poly(vinyl alcohol)/maleic anhydride/acryloyl thioamide monomer (PVA/MA/ATM) photo-cured nanofiber membranes and pure PVA nanofiber membranes were produced by the electrospinning technique. *In situ* UV radiation was applied during the electrospinning in order to provide polymerization during the jet flight and promote crosslinking of ATM and MA with PVA. The cross-linking was examined by Fourier transform infrared spectroscopy (FTIR). The morphology of the electrospun nanofibers was characterized by scanning electron microscope (SEM). The surface area of the nanofiber membranes was measured by Brunauer–Emmert–Teller (BET) analysis. Furthermore, their water durability was examined. The water durability test demonstrated that the *in situ* photo-cured PVA/MA/ATM nanofiber membrane had the lowest average mass loss. The surface areas of PVA/MA/ATM nanofiber membranes were 160–280 m² g⁻¹. The surface area and diameter of PVA/MA/ATM nanofibers decreased with increasing PVA content. The diameter of the obtained nanofibers was less than 100 nm. The results showed that water-insoluble nanofiber membranes with good chemical and thermal resistance were obtained. These nanofiber membranes may be promising candidates for usage in water treatment.

Keywords: electrospinning; nanofiber membrane; poly(vinyl alcohol); photo-curable; thioamide.

INTRODUCTION

Nanofibers are an exciting new class of materials that have been extensively studied due to their uniquely light weight, high porosity, small inter-fiber pore size, large surface area and well-modified surface properties.^{1,2} Many potential

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applications for nanofibers, such as tissue engineering, sensors, biomaterials, device wipes, electrical applications, wound dressings material and filtrations and adsorptions, have been proposed and investigated.^{3–9}

In recent years, electrospinning has become the most common technique for the generation of nanofibers because it is comparatively simple, convenient, effective, low cost and with a relatively high production rate.¹⁰ However, most important is that nanofibers with a diameter in the range of 100–1000 nm could be achieved by electrospinning. This technique has three basic components, *i.e.*, a syringe pump, a high voltage supply and a collector. In the process, a polymer solution or melt is placed into the syringe with a millimeter size nozzle and is subjected to a high voltage. Under the applied electrostatic force, the polymer is ejected from the nozzle, the diameter of which is reduced significantly, as it is transported to and deposited on a collector, which also serves as the ground for the electrical charges.^{11–14}

Poly(vinyl alcohol) (PVA) is a water-soluble, non-toxic and biocompatible polyhydroxy polymer with good chemical and thermal stability.^{15,16} However, the aqueous solubility PVA would limit its use for water treatment.¹⁵ Therefore, when fabricated for aqueous applications, such as filtration and adsorption (*i.e.*, water treatment), PVA must be modified to minimize swelling in water.^{17,18} The most popular way of decreasing the solubility of PVA in water is to crosslink the polymer.

The main purpose of this study was to produce a water-insoluble PVA nanofiber membrane by the electrospinning technique. Chemical crosslinking of PVA with maleic anhydride (MA) and acryloyl thioamide (ATM) during the electrospinning process was realized by the effects of *in situ* UV radiation. Then the obtained PVA/MA/ATM nanofiber membranes were characterized by FTIR, SEM and BET, and their aqueous stabilities were examined.

EXPERIMENTAL

Reagents

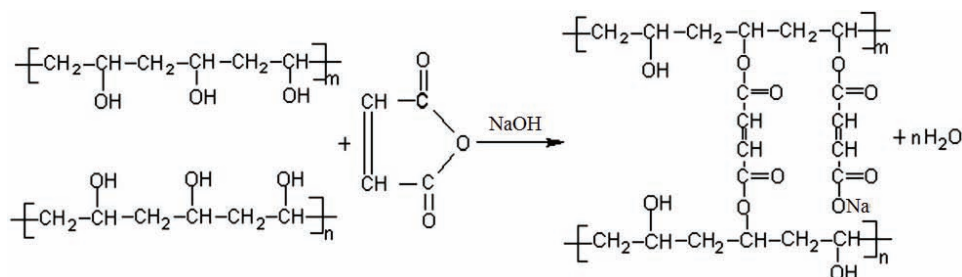
Poly(vinyl alcohol) (PVA; 87–89 % hydrolyzed, \bar{M}_w 146,000–186,000 g mol⁻¹), maleic anhydride (MA), acryloyl chloride (C₃H₃ClO) and the radical photo-initiator, 2-hydroxy-2-methyl-1-phenyl-1-propan-1-one (Darocur[®] 1173), were purchased from Sigma–Aldrich. Thiourea (TU; SC(NH₂)₂), triethylamine (TEA) and dimethylformamide (DMF) were purchased from Merck. Distilled water was used throughout.

Synthesis of acryloyl thioamide monomer (ATM)

Thiourea (0.15 mol) was dissolved in 20 mL DMF at 40 °C and the mixture was charged into a 500 mL three-necked flask fitted with a reflux condenser. After the solution had cooled, TEA (0.15 mol) was added. Then, at 0 °C under nitrogen, acryloyl chloride (0.15 mol) was added slowly drop wise to the reaction mixture under continuous stirring. After 1 h at 0 °C, the reaction was continued at room temperature for an additional 1 h. Then, the solvent was evaporated. The synthesized acryloyl thioamide monomer (ATM) was dried under vacuum at 30 °C for 24 h.

Preparation of the solutions for electrospinning

First, 8, 10 and 12 % PVA solutions were prepared by adding slowly the required amount of PVA powder to distilled water at room temperature. The mixtures were then stirred at 80 °C for 2 h to obtain homogenous solutions and refrigerated overnight to when the solutions become transparent. MA (0.98 g) was added into 50 g of the prepared PVA solutions in the presence of 10 mL of 1 M NaOH with vigorously stirring at 70 °C for 5 h (Scheme 1).



Scheme 1. The esterification reaction between PVA and MA.

Then, the synthesized ATM and Darocur® 1173 as a photo initiator were added at 3 wt. % of the total weight for all formulations and then immediately electrospun. The composition of all nanofiber membrane formulations are given in Table I.

TABLE I. The composition of the formulations used in the synthesis of nanofiber membranes; PVA solution: 50 g

Formulation	MA g	ATM g	Darocur® 1173 %	Sulfur content wt. %	Nitrogen content wt. %
8 % PVA	0	0	0	0	0
	0.98	1.53	3	0.72	0.63
10 % PVA	0	0	0	0	0
	0.98	1.53	3	0.72	0.63
12 % PVA	0	0	0	0	0
	0.98	1.53	3	0.72	0.63

Synthesis of nanofiber membranes

The schematic diagram of electrospinning process combined with UV radiation is shown in Fig. 1. The prepared solution was placed in the syringe. The negative terminal of the high

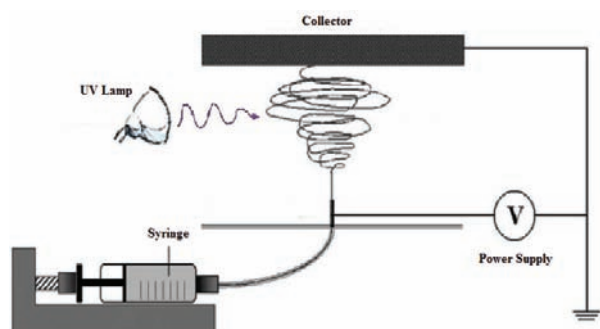


Fig. 1. Schematic diagram of the electrospinning process.

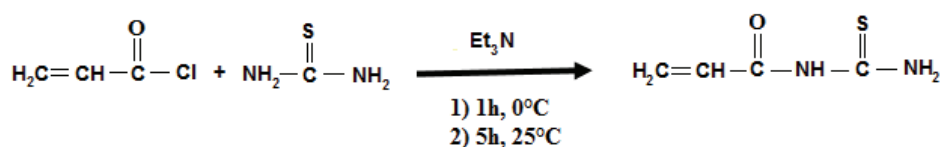
voltage power supply was connected to a conductive drum covered with aluminum foil, which functioned as the collector for the fibers. The positive terminal was connected to the metallic syringe tip. A voltage of 25 kV with a tip-to-target distance of 15 cm at a speed of 0.1 mL h⁻¹ was applied to the solution that was simultaneously radiated with a high pressure UV lamp ($\lambda_{\text{max}} = 365$ nm, OSRAM 300W) and the nanofiber membranes were collected on the aluminum foil. After preparation, the nanofiber membranes were dried for 12 h at 100 °C and then refluxed in ethanol/HCl (mole ratio 10:1) for 24 h at 70 °C to remove the template. Finally, the nanofibers were dried for 6 h at 30 °C under vacuum.

Characterization

The infrared spectra of the prepared membranes were obtained on an FTIR spectrometer (Spectrum 100, PerkinElmer) in the wave number region of 4000–400 cm⁻¹ to define the characteristic peaks of the functional groups of the nanofiber membranes. The surface morphology of the electrospun nanofiber was examined with an SEM (JEOL JSM 7000F). The specific surface area and pore volume were determined using BET analysis (ASAP 2020). In the water durability test, the nanofiber membranes were treated with boiling water for 1 h and the mass loss measured.

RESULTS AND DISCUSSION

ATM was synthesized by reaction between thiourea and acryloyl chloride and the representation of this reaction is shown in Scheme 2. The FTIR spectrum of ATM is given in Fig. 2. According to the spectrum, thioamide group showed an absorption band at 3528 cm⁻¹, due to –NH– stretching of the amide group. The carbonyl stretching of the amide appeared at 1658 cm⁻¹. The C=S group of thioamide showed a band at 1255 cm⁻¹. The peaks at 1089 and 1384 cm⁻¹ are attributed to –C–N groups. Furthermore, –C–H stretching bands were recorded at 2857 and 2928 cm⁻¹. FTIR spectral measurements confirmed the structure of ATM.



Scheme 2. Proposed structure of the synthesized acryloyl thioamide monomer (ATM).

FTIR spectra of the synthesized 10 % PVA and 10 % PVA/MA/ATM nanofiber membranes are given in Fig. 3. The FTIR spectrum of pure PVA nanofiber (Fig. 3a) showed a broad peak at 3307 cm⁻¹ attributed to the hydroxyl (–OH) and at 2910 cm⁻¹ that is due to –CH₂ asymmetric stretching. The peak observed at 1731 cm⁻¹ indicated the (–C=O) carbonyl stretching bond.^{16,18} As shown in Fig. 3b, an absorption band at 1661 cm⁻¹ due to –C=O stretching of the amide group and a carbonyl stretching (–O–C=O) at 1730 cm⁻¹, a C=S stretching bands at 1247 cm⁻¹ and a –C–N stretching bands at 1091–1375 cm⁻¹ were found.^{19,20} The proposed structure of the synthesized PVA/MA/ATM nanofiber membrane is given in Scheme 3.

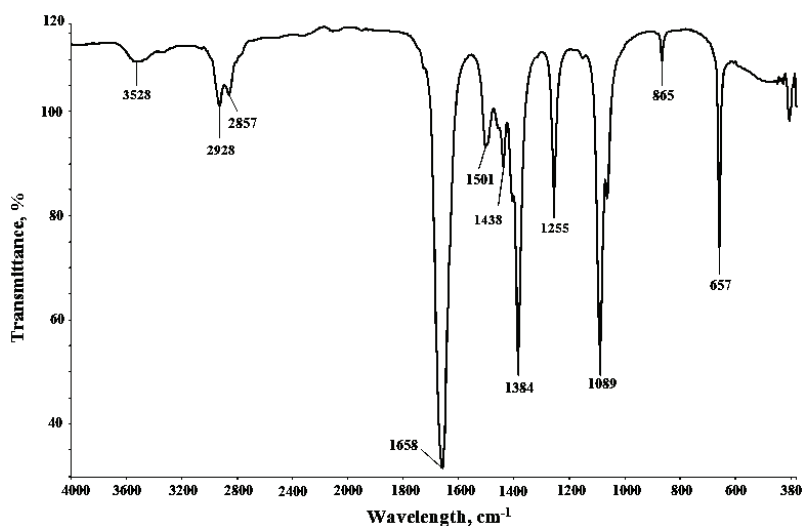


Fig. 2. FTIR spectrum of ATM.

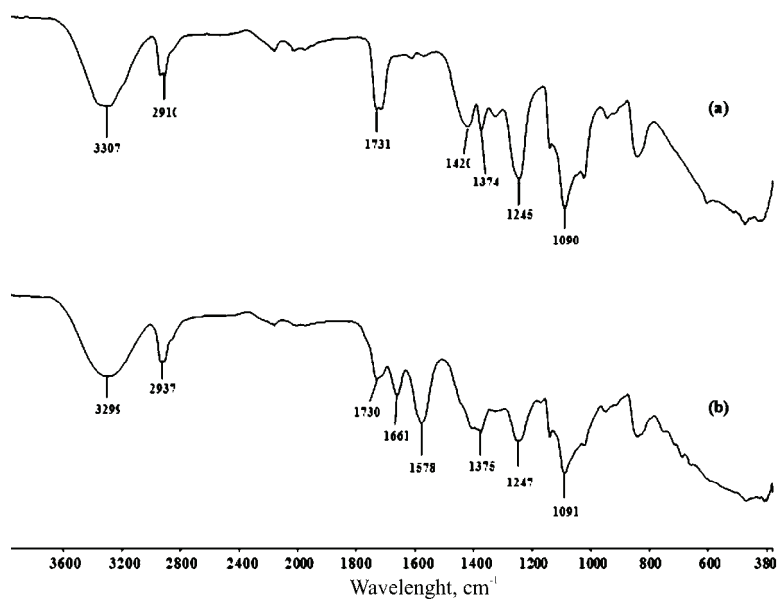


Fig. 3. FTIR spectra of a) 10 % PVA and b) 10 % PVA/MA/ATM nanofiber membranes.

The water durability test involved boiling the synthesized pure PVA, PVA/MA and PVA/MA/ATM nanofiber membranes in water for 1 h. The average mass losses are given in Table II. As seen from the results, pure PVA nanofiber membranes dissolved completely in a short period at room temperature. However, when PVA was crosslinked with dianhydride and thioamide groups, the

resulting PVA/MA/ATM nanofiber membranes were slightly soluble during boiling in water for 1 h. This was mainly due to the efficient crosslinking of PVA with MA and ATM by exposure to UV radiation during electrospinning. Compared to the 8 % PVA/MA/ATM and 12 % PVA/MA/ATM nanofiber membranes, the 10 % PVA/MA/ATM nanofiber membrane had the lowest average mass loss because of being the most efficiently crosslinked. This could be due to the non-efficient crosslinking for the 8 % and the dissolving of unreacted MA for the 12 % PVA/MA/ATM fibers. Yang *et al.*²¹ prepared PVA/MA crosslinked nanofiber membrane by electrospinning directly. In the present work, the thioamide nanofiber membranes were prepared by simultaneously electrospinning and UV radiation. It was found that this method enabled more efficient crosslinking due to photopolymerization and less water-soluble the obtained nanofiber membranes were less soluble.

TABLE II. Physical properties of nanofiber membranes

Nanofiber membrane	Water solubility, %	Surface area, m ² g ⁻¹	Nanofiber diameter, nm
8 % PVA	Soluble	57.72	106–126
10 % PVA	Soluble	48.89	163–190
12 % PVA	Soluble	38.91	236–259
8 % PVA/MA/ATM	3.84	282.71	91–96
10 % PVA/MA/ATM	1.09	225.48	126–134
12 % PVA/MA/ATM	1.83	161.94	244–326

The morphologies of nanofiber membranes and the nanofiber diameters were determined by SEM analysis and the SEM images are shown in Fig. 4. It could be seen that the membranes were composed of numerous, randomly oriented nanofibers. The diameters of the nanofibers increased with increasing amount of PVA. The pure PVA nanofibers were smooth and uniform with diameters in the range of 106–259 nm. The diameters of the 8 % PVA nanofibers were between 106 and 126 nm while diameters of 10 % PVA and 12 % PVA nanofiber were between 163–190 nm and 236–259 nm, respectively (Fig. 4A–C). With the introduction of the dianhydride and thioamide groups to PVA, the nanofibers became more intertwined and there were more crosslinks between the fibers (Fig. 4D–F). As a result, the fiber scaffold became stronger. The diameters of PVA/MA/ATM nanofibers were smaller than those of the corresponding pure PVA fibers. The diameters of the 8 % PVA/MA/ATM nanofibers were less than 100 nm. As the PVA content increased in modified membranes, the diameters increased from 90 to 326 nm, as in the pure PVA nanofiber membranes. It should be noted that the addition of MA and ATM may have caused a possible increase in the conductivity of the solution.⁵ However, there were some beads in the PVA/MA/ATM nanofiber membranes, especially in the 12 % PVA/MA/ATM nanofiber membrane. Furthermore, the Brunauer–Emmet–Teller (BET) surface area values of

nanofibers indicated that the surface area decreased with increasing amount of PVA. The nanofiber diameters and surface areas are given in Table II.

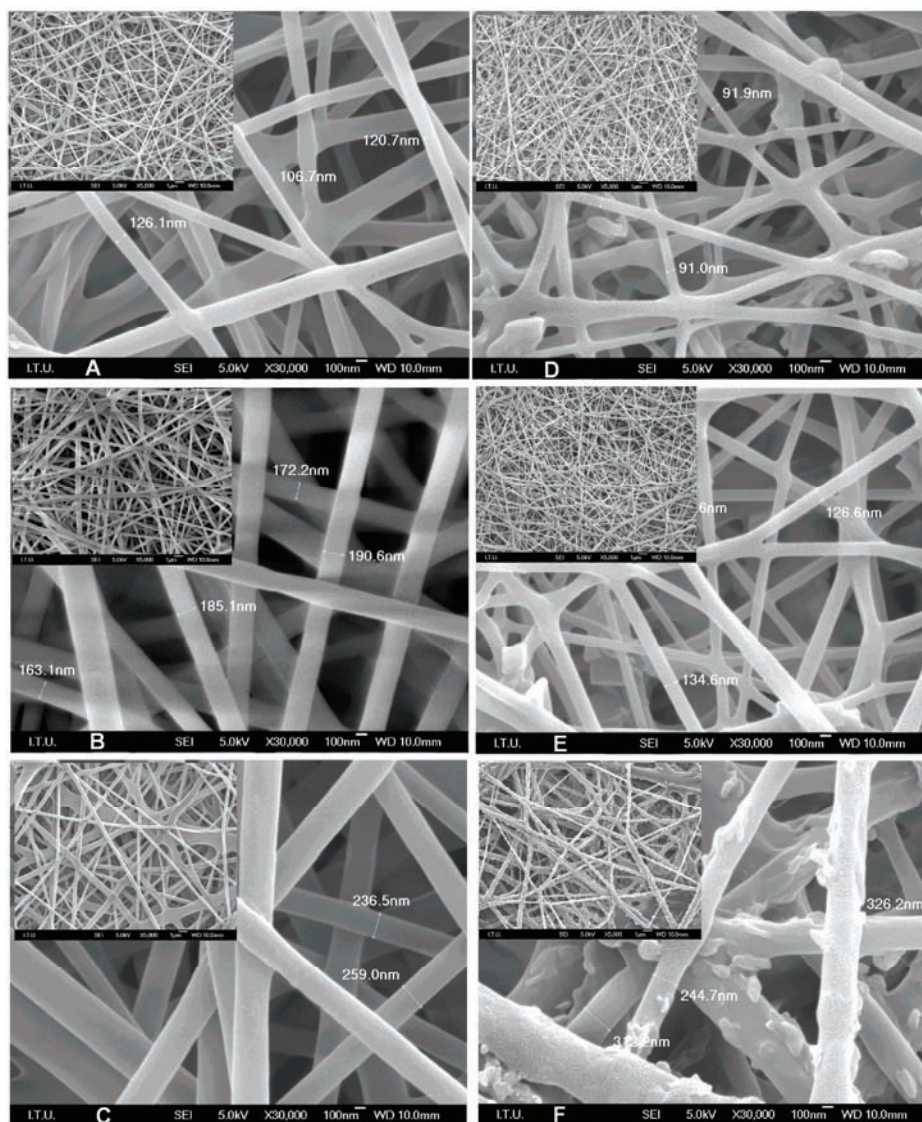


Fig. 4. SEM images of: A) 8, B) 10 and C) 12 % PVA; D) 8, E) 10 and F) 12 % PVA/MA/ATM nanofiber membranes.

CONCLUSIONS

The aim of this study was to synthesize more dynamic nanofiber membranes by combining the electrospinning technique with UV radiation. Photo-crosslink-

ing of the thioamide-functionalized fibers was successfully achieved. Moreover, the effect of PVA content on the properties of the synthesized photo-cured nanofiber membranes was investigated. While pure PVA nanofiber membranes completely dissolved in water, the photo-cured membranes resisted hot water. SEM images showed that the diameters of the nanofibers ranged from 90 to 320 nm and increased with increasing content of PVA. The diameters of the PVA/MA/ATM nanofibers in membranes were smaller than those of the pure PVA nanofibers and their BET surface area was larger. When compared to pure PVA nanofiber membranes, they were tougher and insoluble membranes, had lower fiber diameter and higher surface area. The results illustrated that these photo-crosslinked thioamide functionalized nanofiber membranes possess an enormous potential with the chemical resistance for usage in water treatment as, for example, adsorption media.

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ИЗВОД

УТИЦАЈ САДРЖАЈА ПОЛИ(ВИНИЛ-АЛКОХОЛА) НА ПОСТУПАК ИЗРАДЕ МЕМБРАНА
IN SITU ФОТО-УМРЕЖАВАЊЕМ НАНОВЛАКАНА ФУНКЦИОНАЛИЗОВАНИХ
ТИОАМИДОМБИХТЕР ZEYTUNCU¹, МЕНМЕТ НАКАН MORCALI², SULEYMAN AKMAN³ и ONURALP YUCEL²

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У овом раду је приказано добијање мембрана поступком електроспининга чистих PVA нановлакана као и *in situ* фото-умрежавањем поли(винил-алкохол)/анхидрид малеинске киселине/акрилоил-тиоамид мономера (PVA/MA/ATM). Примена *in situ* UV зрачења у поступку електроспининга омогућава да се реакција умрежавања ATM и MA са PVA одиграва истовремено са формирањем влакана. Ток реакције умрежавања је праћен помоћу инфрацрвене спектроскопије (FTIR). Док су морфологија и термичка својства добијених нановлакана анализирана сканирајућом електронском микроскопијом (SEM). Специфична површина нановлакана добијених мембрана је одређена помоћу Брунауер–Емерт–Телер (BET) методе. Затим је анализирана отпорност нановлакана на воду. Тестови отпорности на воду су потврдили да мембране фото-умрежених PVA/MA/ATM нановлакана показују најмањи губитак масе. Специфична површина PVA/MA/ATM нановлакана у мембранама је износила 160–280 m² g⁻¹. Установљено је да специфична површина и пречник нановлакана опадају са порастом садржаја PVA у полазном раствору. Пречник добијених нановлакана је био мањи од 100 nm. Резултати су потврдили да се овим поступком могу добити мембране од водонерастворних PVA

нановлакана са бољом хемијском и термичком отпорношћу. Мембране сачињене од умрежених PVA нановлакана могу наћи примену у поступцима за пречишћавање вода.

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