

Preparation and Characterization of UV-Cured Hybrid Polyvinyl Alcohol Nanofiber Membranes by Electrospinning

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The present study investigated the possibility of preparing polyvinyl alcoholic (PVA) organic-inorganic hybrid nanofiber membranes by electrospinning with UV irradiation. To this end, PVA, PVA/SiO₂ organic-inorganic hybrid obtained with Geniosil® XL 33 as a SiO₂ source, and imidazole-functionalized mesoporous PVA/SiO₂/N=N nanofiber membranes were synthesized. These membranes were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric-differential thermal analysis, and Brunauer–Emmett–Teller analysis. According to results, fine polymeric nanofibers were obtained in the size range of 100-200 nm for pure PVA nanofibers and 150-250 nm for PVA/SiO₂ hybrid nanofibers, while imidazole-functionalized PVA/SiO₂ nanofibers were less than 100 nm. The membranes produced are suitable for use in various applications, including filtration and adsorption, in the biomedical and textile industries, among others.

Keywords: *electrospinning, nanofiber, UV-curable, hybrid material, polyvinyl alcohol*

1. Introduction

During the past decade, nanofiber has received extensive use in diverse industrial applications because of its extraordinary properties, including its light weight, large surface-area-to-volume ratio, porous structure, and superior mechanical properties¹⁻⁴. Recent developments to improve the chemical properties in nanofiber technology have laid the foundation for current opportunities to revolutionize the material by combining the desirable properties of organic polymers (e.g., elasticity and processability) and inorganic solids (e.g., chemical inertness and thermal resistance)⁵. By combining all of the above properties, organic-inorganic hybrid nanofiber can be used in various products, such as textiles, optical devices, membranes, sensors, tissue engineering scaffolds, and catalytically synthesized nanofiber, among others⁶.

PVA is a semi-crystalline hydrophilic polymer with good chemical and thermal stability. It is a highly biocompatible, highly water-permeable, nontoxic polymer that can be easily processed. Furthermore, PVA is known to interact with other organic and inorganic materials⁵. PVA with functional groups is useful in practical investigations of functional polymers given its easy preparation as a bulk material and in films and fibers⁷⁻⁹. PVA interacts with other materials in electrode position to form a mixed membrane within a polymer matrix. At high temperatures, mesoporous PVA/silica nanofiber membranes can be synthesized;

however, such temperatures remove the organic groups from the matrix, which renders the nanofiber membranes unsuitable for application in water treatment¹⁰⁻¹³.

Electrospinning is a simple, inexpensive, convenient, effective, and widely used technique for generating nanofiber membrane materials that has recently attracted a great deal of attention. In electrospinning, a strong electrostatic force produced by high static voltage is used to create an electrically charged jet of polymer solution that should be placed in a container with a nozzle 1 mm in diameter. During the process, an oppositely charged supply is connected to the needle and grounded collector plate, and as the magnitude of voltage rises, the hemispherical surface of the liquid lengthens to form a Taylor cone and to produce fiber with nano dimensions. After critical voltage is applied, the electrostatic force overcomes the surface tension, and the charged jet is ejected from the tip of the Taylor cone, which undergoes a process of elongation and evaporation that produces polymer nanofiber^{11,14-16}.

This study sought to synthesize an effective nanoscale fiber membrane by electrospinning with UV irradiation and, in the process, compare the three organic-inorganic hybrid nanofiber membranes, the optimal conditions for which this paper reports. To this end, pure PVA nanofiber membrane was compared to both PVA/SiO₂ and imidazole-functionalized (PVA/SiO₂/N=N) hybrid nanofiber membranes, all of which were evaluated by

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Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric-differential thermal analysis (TG-DTA), and Brunauer–Emmett–Teller (BET) analysis.

2. Material and Methods

2.1. Experimental procedures

PVA (87–89% hydrolyzed, Mw 146000–186000 g; Sigma–Aldrich, St. Louis, MO, USA), *N*-vinylimidazole (NVI; Alfa Aesar, Ward Hill, MA, USA), and, as a SiO₂ source, methacryloxymethyltrimethoxysilane (MMTMS; Geniosil® XL 33, Wacker Chemie AG, Munich, Germany) were used in this study, as well as radical photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propan-1-one (Darocur® 1173, Aldrich–Sigma) and both hydrochloric acid and ethyl alcohol (Merck, Whitehouse Station, NJ, USA). Deionized (DI) water was also used throughout the study.

2.2. Preparation of PVA spinning solutions

10 wt.% PVA solutions were prepared by dissolving PVA in deionized water to obtain the ideal thin and uniform PVA fiber¹⁸. PVA powder was slowly stirred into the deionized water at room temperature for 30 min. The temperature was next gradually raised to 85 °C while the mixture was constantly stirred for 3 h to homogenize the solution. The transparent solutions obtained were refrigerated overnight. Next, MMTMS (0.023 mol) and NVI (0.023 mol) were vigorously stirred into 50 mL PVA solutions to homogenize the PVA/MMTMS solutions. Upon adding 3 wt% Darocur® 1173 as a photoinitiator into the prepared solutions, the solutions were immediately electrospun. The components of all nanofiber membranes appear in Table 1.

2.3. Preparation of nanofiber membranes

The prepared solutions were loaded separately into a syringe, to which the positive terminal of a high-voltage power supply was connected, while the negative terminal was connected to a conductive drum covered with aluminum foil as a fiber collector. A voltage of 20 kV with a tip-to-target distance of 15 cm at a flow rate of 3 mL/h was applied to the solution being irradiated with a high pressure UV lamp ($\lambda_{\text{max}} = 365 \text{ nm}$, OSRAM 300w.). During the electrospinning process (Figure 1), a dense web of fibers was collected on the aluminum foil and first dried for 12 h at 100 °C in a vacuum. The nanofiber membranes obtained were refluxed in ethanol/HCl (molar ratio 10:1) for 24 h at 70 °C to remove the template and finally dried for 6 h at 30 °C in a vacuum.

2.4. Characterization

FTIR spectrum of prepared membranes was obtained with FTIR spectrometer (Spectrum 100, PerkinElmer, Waltham, MA, USA) in the wave number region of 4000–400 cm⁻¹ to define the characteristic peaks of functional groups of the nanofiber membranes. The surface morphology of the electrospun nanofiber was examined with SEM (JEOL JSM 7000F). The specific surface area and pore volume were determined using BET analysis (ASAP 2020). The thermal behavior of the PVA based fibers was

Table 1. The components of raw materials used in the synthesis of nanofiber membranes.

Gels	10 Wt.% PVA (g)	MMTMS (g)	NVI (g)	Darocur® 1173 (g)
PVA	50	0.023	0.00	3
PVA/SiO ₂	50	0.023	0.00	3
PVA/SiO ₂ /N=N	50	0.023	0.023	3

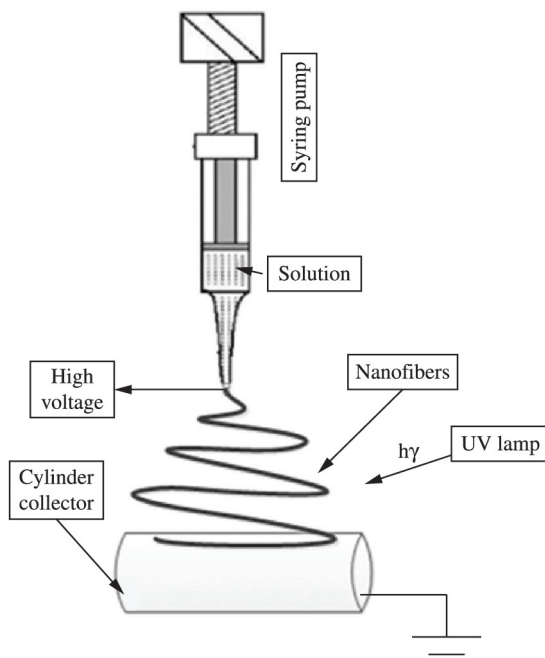


Figure 1. Schematic diagram of electrospinning process.

evaluated by TG-DTA (Diamond TG-DTA, PerkinElmer). Nanofiber membranes were heated from 30 to 750 °C at a rate of 10 °C/min under air.

3. Results and Discussion

UV irradiation nanofibers were prepared by electrospinning under UV irradiation at a voltage of 20 kV with a tip-to-target distance of 15 cm and flow rate of 3 mL/h. They were subsequently extracted with ethanol/HCl (molar ratio 10:1) for 24 h.

Figure 2 shows the FTIR spectra for the pure PVA nanofiber, PVA/SiO₂ nanofiber, and the imidazole-functionalized hybrid nanofiber (PVA/SiO₂/N=N). The FTIR spectrum of pure PVA nanofiber (Figure 2a) exhibited a very strong, broad peak at 3300 cm⁻¹, given the hydroxyl (OH), and at 2942 cm⁻¹, given CH₂ asymmetric stretching. The peak observed at 1088 cm⁻¹ was attributed to the presence of terminal polyvinyl groups, while 1735 cm⁻¹ indicated the carbonyl(C=O) stretching bond^{5,17}. In the FTIR spectrum of PVA/SiO₂ nanofiber (Figure 2b), the bonds recorded at 941 and 1100 cm⁻¹ derived from vibrations of Si–O and Si–O–Si stretching. The peak at 1248 cm⁻¹ was due to Si–CH₂, and the vibration of C=O appeared at 1724 cm⁻¹^{15,18–20}. The FTIR

spectrum in Figure 2c shows the characteristic bands for imidazole group vibrations at 1639 cm^{-1} (C=N stretching), 1248 cm^{-1} (C-N stretching in the imidazole ring), and 1116 cm^{-1} (C-N stretching)²¹. FTIR analysis confirmed that the condensation reaction was successfully performed between PVA, MMTMS and NVI.

SEM images of nanofiber membranes appear in Figure 3. As a result of the strong interaction between the inorganic and organic phases, both the spinning behavior and morphology of the hybrid fibers differ significantly from that of pure PVA fiber. Since the morphology of pure PVA nanofiber exhibited a smooth surface, the PVA/SiO₂ with imidazole tended to form beads (Figure 3e and f). By comparison, the PVA/SiO₂/N=N nanofiber was more densely packed. The average diameter of pure PVA nanofiber fell between 100 and 200 nm (Figure 3b), while that of the

PVA/SiO₂ hybrid fell between 150-250 nm (Figure 3d) and that of the PVA/SiO₂/N=N did not exceed 100 nm. Table 2 shows the BET surface area and the pore volume of extracted nanofiber membranes; clearly, both aspects increased as the PVA was modified.

All nanofiber membranes were analyzed by TG-DTA in air reaching $750\text{ }^{\circ}\text{C}$ in order to study their thermal behaviors. Figure 4 presents the TG-DTA curves of the nanofiber membranes 4. For pure PVA nanofiber membrane, the TG curve revealed a peak at $52\text{ }^{\circ}\text{C}$ due to moisture vaporization. The first decomposition temperature ($235\text{ }^{\circ}\text{C}$) coincided with 5% weight loss, after which a rapid weight loss of 83% occurred as the temperature rose to $495\text{ }^{\circ}\text{C}$. Complete decomposition of the nanofiber occurred from 626 to $660\text{ }^{\circ}\text{C}$ with weight losses of 96 and 98%, respectively.

On the DTA curve, endothermic peaks were observed at 289 and $450\text{ }^{\circ}\text{C}$, while exothermic peaks occurred at 50 , 270 , 362 , 434 , and $496\text{ }^{\circ}\text{C}$. There was a sharp, large exothermic peak at $495\text{ }^{\circ}\text{C}$ concurrent with a weight loss of approximately 88%, which indicated the complete decomposition of the nanofiber that agrees with the TG curve (Figure 4)^{22,23}. As shown in Figure 4b, rapid weight loss occurred from 50 to $150\text{ }^{\circ}\text{C}$ in the thermal curves of the PVA/SiO₂ hybrid nanofiber due to the polycondensation of

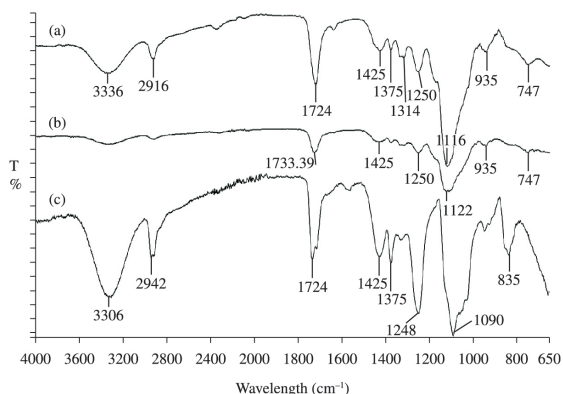


Figure 2. FTIR spectra of (a) PVA, (b) PVA/SiO₂ and (c) PVA/SiO₂/N=N nanofiber membranes.

Table 2. Physical properties of nanofiber membranes.

Nanofiber membrane	Surface area (m ² /g)	Pore volume (cm ³ /g)	Nanofiber diameter (nm)
PVA	30.4	0.031	100-200
PVA/SiO ₂	316.4	0.302	150-250
PVA/SiO ₂ /N=N	386.7	0.365	80-110

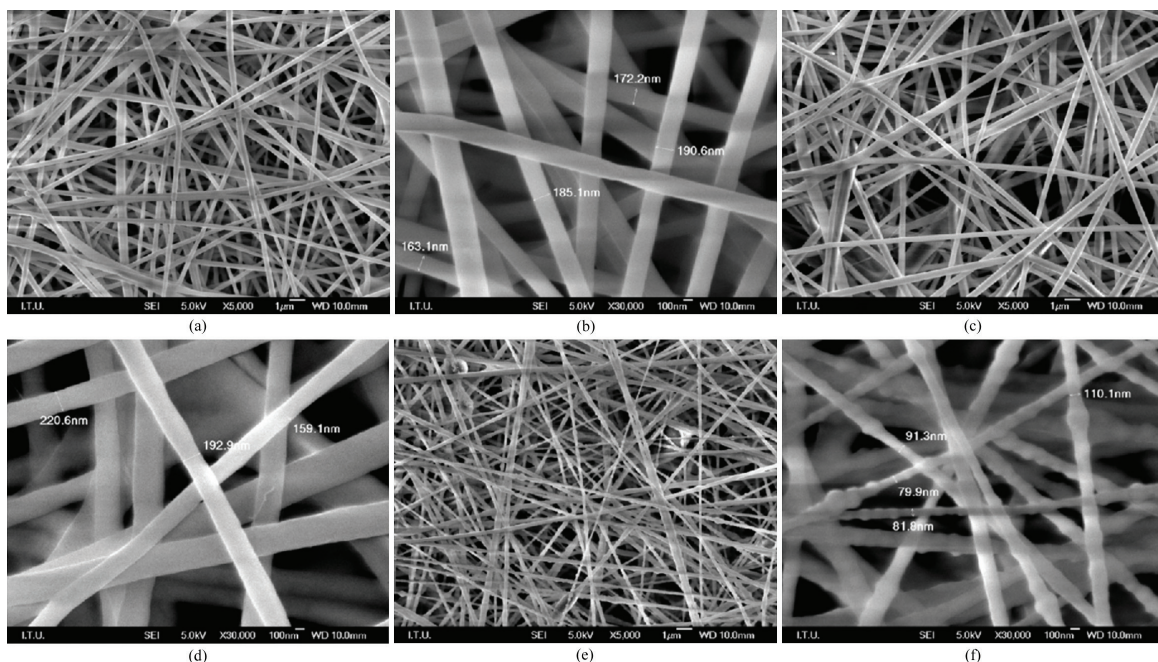


Figure 3. SEM images of (a) and (b) pure PVA nanofiber; (c) and (d) PVA/SiO₂, and (e) and (f) PVA/SiO₂/N=N nanofiber membranes.

the silica matrix. After this point, 85% weight loss slowly occurred as temperatures rose to 540 °C. The last thermal degradation of the organic fraction occurred at 620 °C with a weight loss of 90%. The residue at 620 °C was white, and in this case, no residual carbon was left²⁴.

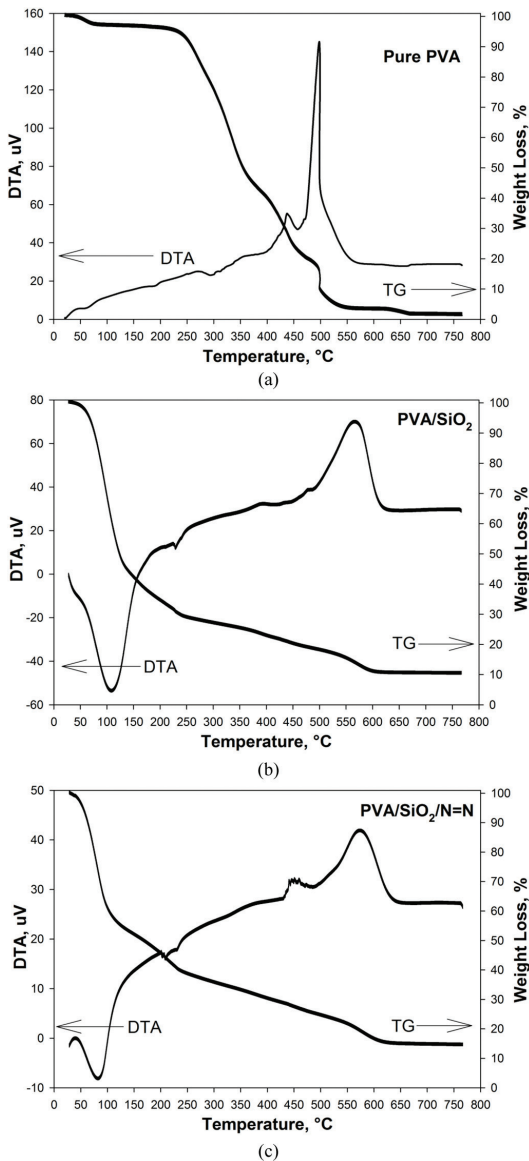


Figure 4. TG-DTA curve of the (a) PVA, (b) PVA-SiO₂, and (c) PVA/SiO₂/N=N nanofiber membranes.

Also on the DTA curve, endothermic peaks were observed at 106, 230, and 485 °C, while exothermic peaks occurred at 221, 390, 478, and 565 °C. As shown in Figure 4c, The PVA/SiO₂/N=N hybrid nanofiber membrane exhibited large thermal degradations from approximately 100 to 620 °C. The improvement in thermal stability of the composites suggests the prevention of thermal motions of the PVA chains given the cross-linking with the imidazole and silica network. A small endothermic peak on the DTA curve was observed at approximately 80 °C, in addition to a broad exothermic peak associated with weight loss from approximately 100 to 570 °C. Two small exothermic peaks at 450 °C and 572 °C on the DTA curve could be ascribed to the thermal decomposition of PVA/SiO₂/N=N²¹.

4. Conclusion

This study investigated the possibility of PVA organic-inorganic hybrid nanofiber membranes by electrospinning combined with UV irradiation. Nanofiber membranes were synthesized by optimizing electrospinning process parameters. While collected on the aluminum foil at 20 kV, the distance between capillary and collecting drum optimized at 15 cm and a flow rate of 3 mL/h for spinning. FTIR analysis confirmed the presence of SiO₂ and an imidazole ring in the membrane, as well as the formation of a PVA/SiO₂/N=N membrane. SEM images revealed that the average diameter of nanofiber in PVA membranes were greater than that in the modified PVA nanofiber membranes. The thermal stability of the nanofiber membranes was assessed by TG-DTA analysis; these membranes achieved thermal stability at approximately 450 °C.

The hybrid nanofiber membranes, which have a mesoporous structure and both a large surface area and pore volume, have better physical and chemical properties than pure PVA nanofiber. Consequently, the membranes produced are suitable for use in various industrial applications, including filtration and adsorption, in the biomedical and textile industries, among others.

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References

- Dzenis Y. Spinning continuous fibers for Nanotechnology. *Science*. 2004; 304:1917-1919. PMID:15218134. <http://dx.doi.org/10.1126/science.1099074>
- Zhang DM and Chang J. Electrospinning of Three-Dimensional Nanofibrous Tubes with Controllable Architectures. *Nano Letters*. 2008; 8:3283-3287. PMID:18767890. <http://dx.doi.org/10.1021/nl801667s>
- Aluigi A, Corbellini A, Rombaldoni F and Mazzuchetti G. Wool-derived keratin nanofiber membranes for dynamic adsorption of heavy-metal ions from aqueous solutions. *Textile Research Journal*. 2013; 83(15):1574-1586. <http://dx.doi.org/10.1177/0040517512467060>
- Feng C, Khulbe KC, Matsuura T, Tabe S and Ismail AF. Preparation and characterization of electro-spun nanofiber membranes and their possible applications in water treatment. *Separation and Purification Technology*. 2013; 102:118-135. <http://dx.doi.org/10.1016/j.seppur.2012.09.037>
- Wu S, Li F, Wang H, Fu L, Zhang B and Li G. Effects of poly(vinyl alcohol) (PVA) content on preparation of novel thiol-functionalized mesoporous PVA/SiO₂ composite nanofiber membranes and their application for adsorption of heavy metal ions from aqueous solution. *Polymer*. 2010; 51:6203-6211. <http://dx.doi.org/10.1016/j.polymer.2010.10.015>
- Hota G, Kumar BR, Ng WJ and Ramakrishna S. Fabrication and characterization of a boehmite nanoparticle impregnated electrospun fiber membrane for removal of metal ions. *Journal of Materials Science*. 2008; 43(1):212-217. <http://dx.doi.org/10.1007/s10853-007-2142-4>
- Lee HW, Karim MR, Ji HM, Choi JH, Ghim HD, Park SM et al. Electrospinning fabrication and characterization of poly(vinyl alcohol)/montmorillonite nanofiber mats. *Journal of Applied Polymer Science*. 2009; 113:1860-1867. <http://dx.doi.org/10.1002/app.30165>
- Galya T, Sedlarik V, Kutritka I, Novotny R, Sedlarikova J and Saha, P. Antibacterial poly(vinyl alcohol) film containing silver nanoparticles: preparation and characterization. *Journal of Applied Polymer Science*. 2008; 110:3178-3185. <http://dx.doi.org/10.1002/app.28908>
- Hong KH. Preparation and properties of electrospun poly(vinyl alcohol)/silver fiber web as wound dressings. *Polymer Engineering and Science*. 2007; 47(1):43-49. <http://dx.doi.org/10.1002/pen.20660>
- Sang YM, Li FS, Gu QB, Liang CZ and Chen JQ. Heavy metal-contaminated groundwater treatment by a novel nanofiber membrane. *Desalination*. 2008; 223:349-360. <http://dx.doi.org/10.1016/j.desal.2007.01.208>
- Haider S and Park SY. Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution. *Journal of Membrane Science*. 2009; 328:90-96. <http://dx.doi.org/10.1016/j.memsci.2008.11.046>
- Demir MM, Özen B and Özcelik S. Formation of Pseudoisocyanine J-Aggregates in Poly(vinyl alcohol) Fibers by Electrospinning. *The Journal Physical Chemistry B*. 2009; 113:11568-11573. PMID:19845394. <http://dx.doi.org/10.1021/jp902380n>
- Peng Q, Sun XY, Spagnola JC, Saquing C, Khan SA and Spontak RJ. Bi-directional Kirkendall Effect in Coaxial Microtube Nanolaminate Assemblies Fabricated by Atomic Layer Deposition. *ACS Nano*. 2009; 3:546-554. PMID:19222233. <http://dx.doi.org/10.1021/nn8006543>
- Shao CL, Kim HY, Gong J, Ding B, Lee DR and Park SJ. Fiber mats of poly(vinyl alcohol)/silica composite via electrospinning. *Materials Letters*. 2003; 57:1579-1584. [http://dx.doi.org/10.1016/S0167-577X\(02\)01036-4](http://dx.doi.org/10.1016/S0167-577X(02)01036-4)
- Taylor G. Electrically Driven Jets. *Proceedings of the Royal Society London Series A*. 1969; 313:453-475. <http://dx.doi.org/10.1098/rspa.1969.0205>
- Mahanta N and Valiyaveetil S. Surface modified electrospun poly(vinyl alcohol) membranes for extracting nanoparticles from water. *Nanoscale*. 2011; 3:4625-4631. PMID:21904762. <http://dx.doi.org/10.1039/c1nr10739a>
- Islam MdS, Karim MR. Fabrication and characterization of poly(vinyl alcohol)/alginate blend nanofibers by electrospinning method. *Colloids and Surface A*. 2010; 366:35-140.
- Sasipriya K, Suriyaprabha R, Prabu P and Rajendran V. Synthesis and characterisation of polymeric nanofibers poly(vinyl alcohol) and poly(vinyl alcohol)/silica using indigenous electrospinning set up. *Materials Research*. 2013; 16(4):824-830. <http://dx.doi.org/10.1590/S1516-14392013005000050>
- Bae JA, Hwang SH, Song KC, Jeon JK, Ko YS and Yim JH. Synthesis of Functionalized Mesoporous Material with Various Organo-Silanes. *Journal of Nanoscience and Nanotechnology*. 2010; 10:290-296. <http://dx.doi.org/10.1166/jnn.2010.1495>
- Sakka S and Almedia RM. Handbook of Sol-gel Science and Technology. In: *Processing, Characterization and Applications*. Massachusetts: Kluwer Academic Publishers; 2005. v. 2, chapt. 7, p. 140-147.
- Thanganathan U. Effects of imidazole on the thermal and conductivity properties of hybrid membrane based on poly(vinyl alcohol)/SiO₂. *Journal of Materials Chemistry*. 2012; 22:9684-9689. <http://dx.doi.org/10.1039/c2jm30975k>
- Mishra R and Rao KJ. On the formation of poly(ethyleneoxide)-poly(vinylalcohol) blends. *European Polymer Journal*. 1999; 35:1883-1894. [http://dx.doi.org/10.1016/S0014-3057\(98\)00283-3](http://dx.doi.org/10.1016/S0014-3057(98)00283-3)
- Rajendran S, Sivakumar M and Subadevi R. Effect of salt concentration in poly(vinyl alcohol)-based solid polymer electrolytes. *Journal of Power Sources*. 2003; 124:225-230. [http://dx.doi.org/10.1016/S0378-7753\(03\)00591-3](http://dx.doi.org/10.1016/S0378-7753(03)00591-3)
- Stefănescu M, Stoia M, Stefănescu O, Davidescu C, Vlase G and Sîrloagă P. Synthesis and characterization of poly(vinylalcohol)/ethylene glycol/silica hybrids. Thermal analysis and FT-IR study. *Revue Roumaine Chimie*. 2010; 55(1):17-23.