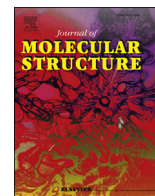




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# Determination of progress in acrylic acid modification on polyvinylidene fluoride membrane by infrared spectroscopy

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## ABSTRACT

Filtration performances of membranes could be improved by blending with organic/inorganic additives or by treating plasma and radiation induced grafting techniques. In this study, acrylic acid (AA) was applied to surface of the polyvinylidene fluoride (PVDF) membrane by chemical grafting method to obtain better membrane materials. Changes were investigated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and contact angle measurement techniques. The presence of the bands indicated acrylic groups and increase at cross section thickness of AA grafted sample after modification confirmed the progress of grafting. Coated skin layer onto membrane surface was seen at the SEM images. Water uptake capacities (WU%) of acrylic acid grafted membrane increased to 64% from 57% of unmodified PVDF relatively with increasing hydrophilicity understood by decreasing contact angles of AA modified samples. By using easy and low cost method, acrylic acid was effectively incorporated on to surface of the PVDF membrane. That is the convenient application to prepare functional structures which contain specific groups on surface of membrane via acrylic molecules in addition to obtain high performance filtration membranes.

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## 1. Introduction

Polyvinylidene fluoride (PVDF) is an organic material which consists of - [CH<sub>2</sub>-CF<sub>2</sub>] - chain order. PVDF is commonly preferred as an industry material in a large scale due to its high chemical, physical and thermal resistance [1]. Main restriction of PVDF as a filtration membrane is that, its hydrophobic structure which prevents water permeation and also causes the organic accumulation. To overcome this drawbacks, incorporation of inorganic materials such as TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO, Fe<sub>3</sub>O<sub>4</sub> or modification of membrane surface with different organic structures by argon or pulsed plasma induced, photo initiating, electron radiation, ozone treating grafting techniques had been applied for two decades [2,3]. Poly(ethylene glycol) (PEG), polydopamine, different dopamine-like materials such as 3,4-dihydroxyphenylalanine, lysine, glycine and serine based grafting materials were used to obtain fouling resistance polysulfone (PSf), polytetrafluoroethylene (PTFE) and polydimethylsiloxane (PDMS) surface for better membran filtration [4–6]. Different from blended materials, grafted or coated groups on the surface act as a fouling resistance by physical and energy

barrier properties of them [7]. Grafting initiated by chemical, radiation, photochemical, plasma and enzymatic processes are available [8]. Radiation or plasma induced grafting could provide controlled and atomic level treatment. However their high cost and abrasive effect are one of the side effects of method which restrict application and using area of them. Among mentioned techniques chemically induced surface modification has advantages of easy and fast application procedure in addition to its low cost and effective impact. In this study acrylic acid (AA) was grafted on to PVDF surface by chemical treatment to improve membrane properties. Progress in the application was monitored by FT-IR analysis and performance of membranes were determined at ultrafiltration membrane cell.

## 2. Materials and methods

### 2.1. Modification of PVDF membranes

Polyvinylidene fluoride, PVDF (Solef 6010), *N,N*-dimethylformamide, DMF (73.09 g/mol, 0.944 g/mL Sigma Aldrich), double distilled water was used as solvent, polymer and non-solvent respectively. The polymer solution of PVDF (1.6 g) in DMF (10 mL) as 14% mass ratio in terms of polymer to solvent was

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prepared by stirring the mixture at 250 rpm, 65 °C for 2 h. Membranes were prepared by immersing of dope solution casted on glass plate (15 cm × 15 cm) and stored in water. Prepared PVDF membranes at 300 μm thickness were exposed to mixture of 0.5 mol/L potassium hydroxide (56.11 g/mol, MERCK) and 2% mass ratio potassium permanganate solutions (158.034 g/mol, ALDRICH) at N<sub>2</sub> atmosphere for 15 min. That sample was called as P-1. After that, P-1 was immersed in to mixture of 5% H<sub>2</sub>SO<sub>4</sub> (98.08 g/mol, % 95–98, 1.84 g/mL SIGMA-ALDRICH) and sodium bisulphide (104.06 g/mol, SIGMA-ALDRICH) solutions to obtain active groups on the membrane surface and that was called as P-2. Hydroxide contained sample called as P-2 was waited in acrylic acid/ethylene glycol (72.06 g/mol, %99, 1.05 SIGMA-ALDRICH) at 40 °C for 5 min and that was furnace at 90 °C for 4 h to obtain acrylic acid grafted membrane, P-AA. After heat treatment it was washed with distilled water until obtain completely cleaned membrane from the chemicals and it was stored in pure water for characterization and performance measurements.

## 2.2. Characterization of PVDF and modified PVDF membranes

Progress in surface modification of PVDF membranes were investigated by Perkin Elmer FT-IR device in the region between 4000 and 650 cm<sup>-1</sup>. The surface hydrophilicity of membranes was investigated by contact angle analyzer (KSV Attention, Finland). Membran morphology was investigated after broken in liquid nitrogen by SEM (Carl Zeiss ULTRA Plus, Germany). Concentration of BSA was determined by UV–visible spectrometer (PG instruments, T80) at 280 nm wavelength. Water uptake capacity (WU%) and porosity (P%) of membranes were calculated according to eq. (1) and eq. (2):

$$WU(\%) = \frac{W_w - W_d}{W_w} \times 100 \quad (1)$$

$$P(\%) = \frac{W_w - W_d}{dA\delta} \times 100 \quad (2)$$

Where *d* is the density of water at 25 °C, *A* is membrane area (cm<sup>2</sup>) and *δ* is the thickness of wet membrane (cm), (*W<sub>w</sub>*): mass of wet membrane, (*W<sub>d</sub>*): mass of dry membrane. Pure water flux (PWF, L/m<sup>2</sup>h) performances of membranes were measured at ultra filtration cross flow membrane cell at 200 kPa and it was calculated by eq. (3):

$$PWF = \frac{V}{At} \quad (3)$$

Where *V* is volume of permeate (L), *A* is membrane area in square meter (1.7 × 10<sup>-3</sup> m<sup>2</sup>) and *t* is the sampling time (h). 0.5 g/L aqueous BSA solution as a model pollutant was (0.01 mol/L, pH:7.4) filtered at 200 kPa. Rejection capacity was calculated by eq. (4):

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

Where, *C<sub>p</sub>* and *C<sub>f</sub>* are the concentration of protein in permeate and feed solutions respectively [9]. To analysis the capacity of membranes against accumulation of organic matter, the calculations were done according to eq. (5) and eq. (6):

$$\text{Flux recovery ratio}(FRR\%) = \left(\frac{J_1}{J_0}\right) \times 100 \quad (5)$$

$$\text{Irreversible flux loss}(IFL) = \frac{J_0 - J_1}{J_0} \quad (6)$$

*J<sub>0</sub>* and *J<sub>1</sub>* are the water flux ratios of membranes before and after BSA rejection experiments respectively.

## 3. Results and discussion

### 3.1. Characterization of PVDF and modified PVDF

Infrared spectroscopy was used to determine the functional groups on the PVDF and modified PVDF membranes to obtain information about grafting process. Existence of new bands on IR spectrum of modified samples was attributed to oxidation and grafting of surface. Characteristic CF<sub>2</sub> and CH<sub>2</sub> stretching vibrations could be seen at 839, 1174, 1231 and 1402 cm<sup>-1</sup> respectively [10,11] (Fig. 1). Asymmetric and symmetric CH and CH<sub>2</sub> stretching vibrations for pristine and modified PVDF samples were observed at around 2885, 2984 and 3021 cm<sup>-1</sup> for the all PVDF samples [12–14]. New band emerged at 1710 cm<sup>-1</sup> for the P-AA spectrum was due to C=O groups of acrylic acid grafted. Also the band at 1561 cm<sup>-1</sup> which could be seen with the 1710 cm<sup>-1</sup> band was

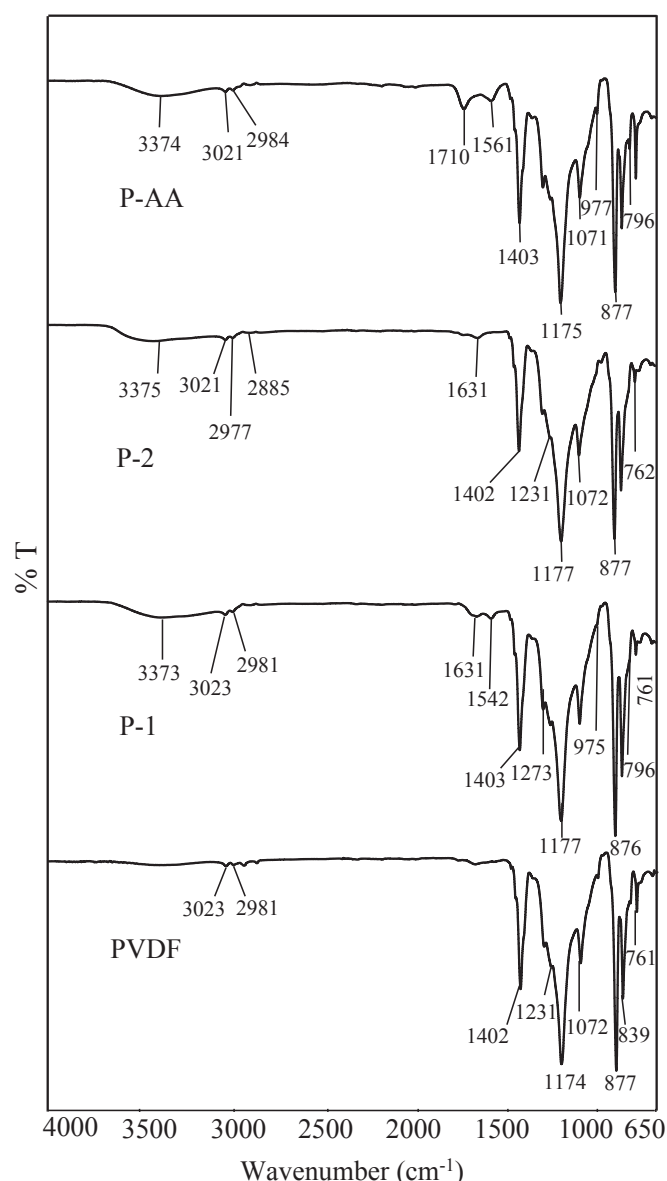


Fig. 1. FT-IR spectra of PVDF and modified PVDF.

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