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Original Article

Graft copolymerization of GMA and EDMA on PVDF to hydrophilic surface modification by electron beam irradiation

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ABSTRACT

This study was carried out to convert the hydrophobic characteristics of PVDF to hydrophilic. Poly(-vinylidene fluorine) (PVDF) was grafted by electron beam irradiation and sulfonated. The grafting degree of modified PVDF increased with the monomer concentration, but not the conversion degree. From the results of FTIR and XPS, it was shown that the amount of converted sulfur increased with the grafting degree. The radiation-induced graft polymerization led to decrease fluorine from 35.7% to 21.3%. Meanwhile, the oxygen and sulfur content increased up to 8.1% and 3.2%. The pore size of modified membranes was shrunken and the roughness sharply decreased after irradiation. The ion exchange capacity and contact angle were investigated to show the characteristics of PVDF. The enhanced ion exchange capacity and lower contact angle of modified PVDF showed that the hydrophilicity played a role in determining membrane fouling. Electron beam irradiation successfully modified the hydrophobic characteristics of PVDF to hydrophilic.

1. Introduction

Fluorine polymers usually show very stable properties because of excellent thermal stablity, chemical resistance and morphological characteristics. The inertness of poly(vinylidene fluoride) (PVDF) has been widely used for many polymeric membrane applications such as wastewater treatment, ion exchange and biomedical technology [1–6]. According to the water shortage in the world, many investigators have paid much attention to the technology for water reuse. Poly(vinylidene fluoride) (PVDF) is one of the most important engineering fluorine polymers such as microfiltration, ultrafiltration and membrane distillation [7–9]. However, its intrinsic hydrophobicity limits practical separation processes to some extent. PVDF is susceptible to hydrophobic substance adsorption and membrane fouling onto membrane surface due to its low surface energy. The dramatic decrease of flux results from the hydrophobic nature [1,7]. To overcome its fouling property, several investigators have taken much notice of improving hydrophilicity and permeation performance of PVDF

membrane. Antifouling is the process of removing or preventing the accumulation of bacteria, proteins, debris and crystals. To prevent fouling or clogging onto the membrane, several hydrophilic polymers, including the hydrophilized PVDF, have been recently developed.

The hydrophilic modification of PVDF can be achieved by various methods such as chemical treatment by dehydro-fluorination, chemical coating by dipping or spraying step and radiation-induced graft polymerization by high energy irradiation. The grafting polymerization by chemicals is a well-established method for surface modification of polymers. However, it is environmentally of concerns and employed to difficult operations in control. Chemical grafting inherently provides potential of hazards associated with several reactive reagents and solvents. Specifically, ultraviolet irradiation needs a toxic photoinitiator. The chemical deposition method requires dry vapour conditions for free radical polymerization of solvents [7,10,11]. In contrast, the radiation-induced graft polymerization by high energy sources such as plasma, gamma-ray and electron beam is a cleaner method. It is possible to modify polymers without chemical by-products. A very strong energy of electron beam generates excellent graft modification of polymer matrix endowed by homogenous reaction and high penetration nature [12–18]. Considerable attention has been paid to hydrophilic modification of PVDF by high energy

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irradiation. Some monomers, such as acrilyic acid/sodium-4-styrenesulfonate [13], poly(acrylic acid) [19], hydroxyethyl acrylate [20], poly(1-N,N-dimethylamino) ethyl methacrylate, poly(2-oligo (ethylene glycol) monomethyl ether methacrylate), poly(2-hydroxyethyl methacrylate) [21], were used for improving the hydrophilicity of PVDF. Radiation grafting changes the surface of polymeric materials by chemically bonding polar or non-polar monomers having functional groups, such as −COOH, −OR, −OH, −NH2, −SO₃H, −R and their derivatives, to affect surface properties without influence on the bulk material. Electron beam radiation can be used to generate active sites (free radicals) on a polymeric surface which can then react with vinyl monomers to form a graft copolymer. A graft copolymer can be defined as branched copolymer composed of a main chain of a polymer backbone onto which side chain grafts (branches) are covalently attached. The polymer backbone may be a homopolymer or copolymer and differs in chemical structure and composition from the graft material [18–21].

In this study, the microfilteration pore sized PVDF membranes were modified by radiation-induced graft polymerization of glycidyl methacrylate (GMA) and ethylenglycol dimethacrylate (EDMA) and functionalization of sulfite groups. The charged PVDF membranes were physicochemically characterized using the data of Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), ion exchange capacity (IEC) and contact angle. Water permeability of modified PVDF was determined to investigate the enhancement of membrane anti-fouling capacity.

2. Materials and methods

2.1. Materials and chemicals

A hydrophobic PVDF, commercially available membrane, used in this study was purchased from Millipore Co. (Middlesex, UK). Average pore size and thickness of commercial PVDF were 0.2 and 100 μm. GMA, EDMA, isopropanol, methanol and sodium sulfite were purchased from Sigma-Aldrich (St. Louis, MO, USA). Isobutanol and sodium hydroxide were purchased from Merck (Darmstadt, Germany). All the reagents used were of analytical grade. Deionized water from Millipore Milli-Q water system (18.2 MΩ/cm) was used throughout the study.

2.2. Grafting GMA/EDMA and sulfonation

Surface modification of PVDF was carried out by electron beam irradiation. The conditions of grafting, washing and immersion method were followed by our previous study [22]. The experimental conditions of each test set for grafting and sulfonation are shown in Table 1. Each PVDF was immersed into a sealed with butyl rubber stoppers bottle (water:methanol = 1:1). GMA and EDMA were added as monomers. After purging with nitrogen gas for 30 min, PVDF membranes were irradiated by electron beam with the dose of 7 kGy. Electron beam irradiation was carried out by an electron accelerator (1 MeV, 10 kW; ELV-4, EB-Tech Co., Korea). The

absorbed dose was measured with dichromate solution according to the method described by Han et al. [23]. After irradiation, the grafted PVDF was washed with a solution (water:methanol = 1:1) and pure methanol several times. To obtain grafting degree (GD), each membrane was prepared at 60 °C for 24 h in a vacuum oven. The grafting degree can be calculated by following equation.

$$GD(\%) = \frac{(W_1 - W_0)}{W_0} \times 100 \qquad (1)$$

where.

GD: grafting degree
W_0: the weight of the raw membrane [M]
W_1: the weight of the grafted membrane [M]

The epoxy groups of GMA onto the grafted membrane were converted into sulfonic functional groups. The radiation-induced graft membranes were immersed into a solution (sodium sulphite:water:isopropanol = wt%10:75:15) at 40 °C for 24 h in a vacuum. The conversion degree from epoxy to sulfonic functional groups can be calculated by following equation.

$$X(\%) = \frac{(W_2 - W_1)}{(W_1 - W_0)} \times \frac{142}{103} \times 100 \qquad (2)$$

where.

X: conversion from epoxy to sulfonic functional groups
W_2: the weight of the sulfonated membrane [M]
142: the molecular weight of GMA [M]
103: the molecular weight of sodium sulfite [M]

2.3. FTIR-ATR

To investigate difference of chemical structure between virgin and modified PVDF, a Fourier transform infrared spectroscopy (Varian, USA) using the attenuated total reflectance mode was employed. The FTIR spectra of PVDF membranes were obtained using a 660-IR spectrometer (Varian, USA).

2.4. XPS

X-ray photoelectron spectroscopy analysis was performed using a VG multilab 2000 spectrometer (ThermoVG scientific, USA) in an ultra high vacuum. This system used an unmonochromatized Mg K$_\alpha$ (1253.6 eV) source and a spherical section analyzer. The accuracy of binding energy values was ± 0.1 eV. For the analysis of XPS peaks, the C1s peak position was set as 284 eV and used as internal reference to locate other peaks. The relative surface atomic ratio was estimated from the corresponding peak areas, corrected with the tabulated sensitivity factors.

2.5. SEM

The morphology of virgin and radiation-induced graft PVDF was investigated using a scanning electron microscopy (JSM-7500F, JEOL, Japan). Prior to SEM experiment, samples were attached by carbon tape and a conductive gold film was deposited on the specimen surface with 25 kV and 10 mA. The voltage of measurement was 20 kV.

Table 1
Experimental conditions of each test set for grafting and sulfonation.

Test set	GMA (w/w%)	EDMA (w/w%)
Virgin	0.0	0.00
Set 1	0.1	0.00
Set 2	0.1	0.02
Set 3	0.5	0.00
Set 4	0.5	0.10

2.6. AFM

Membrane surface roughness and morphology were analyzed by an atomic force microscopy (PUCOStation AFM, Surface Imaging Systems, Germany). The surface AFM images were conducted in non-contact mode with silicon probe (APPNANO, Applied Nano Structures, USA). Membrane surface roughness was quantified by root mean square (RMS) roughness, which is the RMS deviation of the peaks and valleys from the mean plane. Scanned images were analyzed using SPIP software (Surface Imaging Systems, Herzogenrath, Germany). All membranes were scanned three times, and the scan position at each time was randomly selected.

2.7. Ion exchange capacity

Ion exchange capacity of each test set was measured according to Targer et al. [24]. Each membrane was washed with purified water for 15 min and immersed in 1 N HCl for 24 h. The protonated membranes were rinsed with purified water for 30 min and then soaked in 1 N NaCl for 24 h. To determine the concentration of exchanged proton, each test set was titrated with 0.01 N NaOH. The IEC of membrane was calculated as follow;

$$IEC = \frac{(VN)_n - (VN)_b}{m} \quad (3)$$

Where, V and N are the volume and normality of the NaOH spent on the membranes (n) and blank (b), and m is the mass of the dried membrane sample.

2.8. Contact angle

The contact angle of membrane between membrane surface and water was analyzed by the Wilhelmy plate method, and the measurement was carried out using s Sigma 701 microbalance (KSV Instrument Ltd., Finland) interfaced with a PC for automatic control and data acquisition. During the measurement, each membrane was held vertically attached to a microbalance, and a cell of test liquid moved up and down repeatedly at a constant speed. The surface tension of test liquids at each time was measured by the Force Du Nouy ring method under temperature between 20 and 24 °C and humidity between 20 and 25% conditions. The ring was rinsed with deionized water and ethyl alcohol and was cleaned by burning it in red hot flame of a Bunsen burner prior to each test.

3. Results and discussion

3.1. Grafting and sulfite conversion

The radiation-induced graft polymerization by high ionizing energy is known as one of the most effective ways for the introduction of active functional groups into the grafted polymer. Grafting yield and sulfur conversion of each test set is shown in Fig. 1. As shown in Fig. 1a, the grafting degree increased with the GMA concentration. The grafting degree of each test set was 0.7, 0.6, 3.5, and 3.1% corresponded to set 1, set 2, set3, and set 4, respectively. The grafting degree of radiation-induced graft PVDF was proportional to concentration and absorbed dose [25,26]. Meanwhile, the grafting degree decreased with the addition of crosslinker to some extent. In addition, sulfonation of each test set (conversion degree) was determined by the GMA and EDMA concentrations, indicating that the transformed amount of oxirane groups in GMA into sulfonic groups determined the conversion degree (Fig. 1b). The conversion degree of each test set was 99, 97, 98, and 96% corresponded to set 1, set 2, set3, and set 4,

respectively. GMA was used as active monomer, while EDMA was crosslinker in PVDF-g-(GMA-co-EDMA). The crossliking reaction of polymer generates denser structure, resulting in decrease of oxirane groups in the grafted membrane. The higher concentration of closslinker generates lower sulfur degree because sulfur conversion is carried out by nucleophilic substitution reaction of oxirane groups. Oxirane readily reacts with several nucleophiles such as sulfite with opening of the ring via nucleophilic substitution reaction (S_N2 mechanism). In other words, to obtain higher grafting and conversion degree, the lower the EDMA concentration is required in a copolymer. Some investigators reported similar results from GMA/DVB or GMA/EDMA co-grafting [27,28].

3.2. FTIR spectra

After grafting, the polymerized membrane of each test set was sulfonized with sodium sulfite. To investigate the characterization and chemical structure change of virgin and modified PVDF, FTIR analysis was carried out as shown in Fig. 2. The surface modification of PVDF via electron beam was qualitatively characterized in FTIR spectra. The bands at 1068 cm^{-1} is ascribed to the C–H asymmetric [29]. The predominant vibrations are C–H, C–C and C–F deflections at 1200 cm^{-1}. The stretching variation of C=C bond caused by defluorination of C–F bonds is at 1631 cm^{-1} [30]. The characteristics signal of the grafted membrane prior to sulfonation are: C=O bond at 1720 cm^{-1} and C–O–C bond 1140 cm^{-1}. A strong C=O stretching band with the maximum at 1720 cm^{-1} showed the characteristics of GMA grafted membrane, indicating the success of grafting GMA on the membrane surface. The grafted PVDF presents an IR responsive value of –C-O- bond ascribed to hydroxyl functional groups from the absorption of water onto membrane surface [20]. Unlike virgin, it is obviously shown that the characteristic peak for sulfite with absorption at 1056 cm^{-1}. The characteristic peaks for sulfite is attributed at 1030-1060 cm^{-1} [31]. From the results of FTIR, it was shown that PVDF can be successfully modified by radiation-induced grafting and sulfonic conversion. The functionalization with sulfite onto the grafted membrane accounted for the enhanced hydrophilicity and antifouling performance of modified PVDF.

3.3. XPS analysis

The XPS survey scan spectra are shown in Fig. 3. This showed typical PVDF peaks corresponding to C1s (binding energy, 285.4 eV), F1s (binding energy, 687.2 eV) and O1s (binding energy, 533.7 eV). Unlike virgin, modified PVDF showed an additional peak attributed to S2p3 (binding energy, 169.5 eV) and Na1s (binding energy, 1071.5) indicating the presence of sulfite groups. The fluorine peak of virgin sharply decreased and the oxygen peak of each test set increased after electron beam irradiation. Chemical composition of virgin and modified PVDF is shown in Table 2. The change of chemical composition between virgin and modified PVDF clearly indicated successful grafting of monomers and sulfite conversion. The fluorine content of modified PVDF significantly decreased with the monomer addition, coinciding with increase of oxygen and sulfur content. This is mainly due to defluorination of PVDF by electron beam irradiation. It seems that dehydrogenation readily occurs rather than defluorination because dissociation energy (435 kcal/mol) of CH$_3$–H is lower than that (452 kcal/mol) of CF$_3$–H. However, the radiation-induced graft polymerization was carried out by defluorination due to the lower stability of radicals [30,32]. The obvious change of chemical composition was shown at test set 3. As the grafting reaction mainly occurs onto the membrane surface, the satisfactory monomer concentration enhanced the fluorine decrease of the grafted PVDF. It can be noticed that the
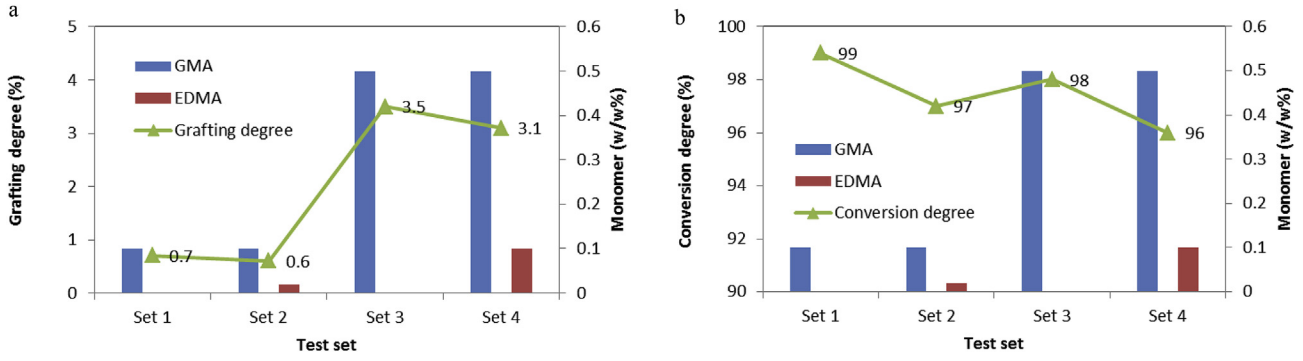
a

b

Fig. 1. Grafting degree and sulfur conversion at each test set (a) grafting degree (b) sulfite conversion.
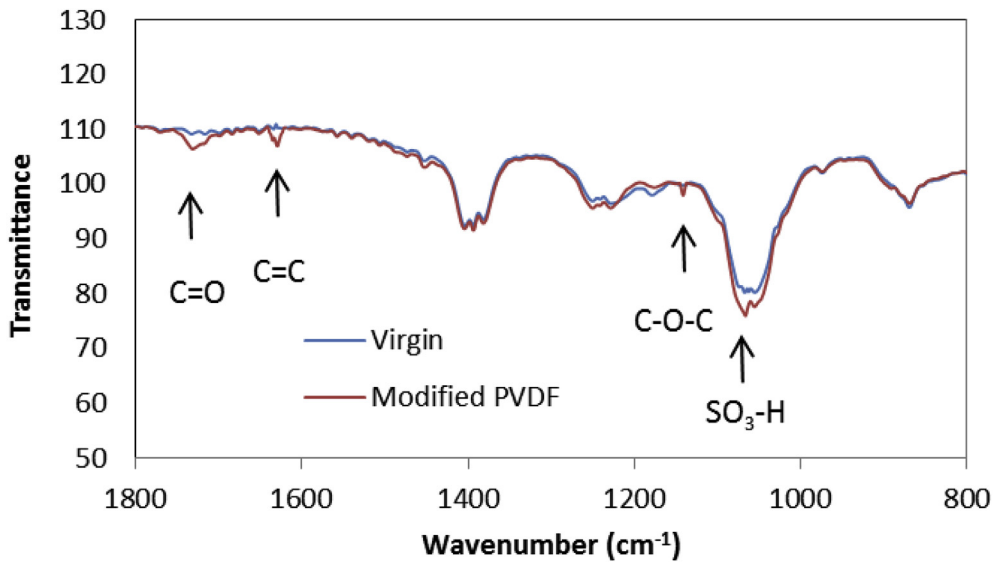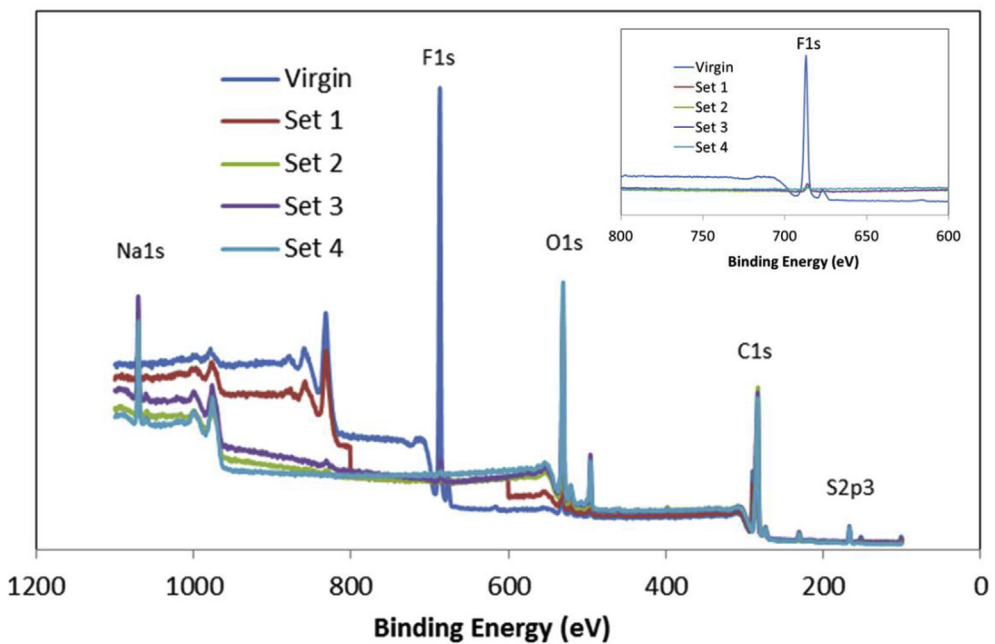

Fig. 2. FTIR spectra of PVDF membranes.

Fig. 3. XPS survey scan spectra at each test set.

Table 2
Chemical composition of virgin and modified PVDF.

Test set	Atom (mol%)				
	C1s	O1s	F1s	Na1s	S2p3
Virgin	64.85	0.32	35.67	0	0
Set 1	65.23	1.57	31.31	1.35	0.78
Set 2	65.45	1.18	32.73	0.68	0.59
Set 3	64.56	8.07	21.30	3.28	3.23
Set 4	66.57	4.06	25.30	3.46	1.40

increase of grafted GMA layer with EDMA was closely related to grafting degree increase and fluorine content decrease. This implies that both active reagent and crosslinker played an important role in decreasing of hydrophobicity. The increased oxygen and sulfur content was attributed to sulfur conversion of oxirane groups. This revealed that the C–C chains in PVDF were functioned as backbones. Meanwhile the C–F chains in virgin became scissile bonds by electron beam irradiation. XPS data, in the agreement with the FTIR results, suggest that grafting and sulfonation successfully enhanced the hydrophilicity of PVDF.

3.4. Surface morphology

The surface morphology change between virgin and modified PVDF are shown in Fig. 4. More edgeless and elliptical pores were observed in the grafted PVDF. Electron beam irradiation enabled pore size to be significantly shrunken. There is no disagreement on the pore size reduction of polymer after high ionizing energy irradiation. Masuelli et al. [33] showed pore size reduction of radiation-induced graft PVDF membranes. The morphology of radiation-induced graft membrane turned to be elliptical, and the pore size was sharply decreased with reaction time and irradiation dose [34]. In addition, membrane surface was changed to denser by radiation-induced graft polymerization. The higher monomer concentration, the denser membrane [35].

The roughness of virgin and modified PVDF was characterized using AFM. The surface AFM images obtained from virgin and modified membrane are presented in Fig. 5. The AFM images show dark depressed valleys or pores and bright nodules of membrane surface. Obvious difference of surface topography was observed between virgin and modified PVDF. The more bright nodules of virgin, the more dark valleys of grafted PVDF. Roughness parameters obtained from AFM images of each test set are shown in Table 3. Roughness of grafted membrane decreased with the monomer concentration. The average arithmetic roughness (Ra) decreased with the monomer concentration, especially the addition of EDMA. In addition, the root mean square average roughness (Rq) showed a similar pattern. This indicates that radiation-induced graft polymerization produces denser structure and polymer plugging on membrane surface caused by filling up to the valley of monomer on the membrane surface [36].

3.5. Ion exchange capacity

The comparison of IEC between virgin and modified PVDF is shown in Table 4. The IEC values of modified membrane of each test set was 0.00, 0.49, 0.44, 1.61, and 1.55 meq/g corresponded to virgin, set 1, set 2, set3, and set 4, respectively. All IECs of sulfonated PVDF were greater than that of virgin. The IEC of modified PVDF increased with GMA concentration, but the addition of EDMA. The grafted PVDF including crosslinker generates denser structure, resulting in the decreased amount of oxirane groups to be converted into sulfonic groups [33].

3.6. Contact angle

The contact angle of membrane surface is usually used to characterize polarity or energy of polymers. The hydrophilicity of membrane is conveniently estimated by measuring its contact angle. The variation of contact angle with grafting degree and oxygen and sulfur content is shown in Table 5. The initial contact angle for virgin was $142.0°$. Wang et al. [36] reported that contact angle of unmodified PVDF membrane was $145.6°$. The contact angle of each test set was 142, 110, 117, 48, and 60° corresponded to virgin, set 1, set 2, set3, and set 4, respectively. The lowest contact angle was shown at test set 3. The contact angle of each test set decreased with the monomer concentration. Liu et al. [13] reported that faster decrease of contact angle was observed in a higher grafting degree membrane. In addition, the decrease of contact angle was mainly caused by the increase of oxygen and sulfur content. The O/C and S/C atomic ratio of each test set was 0.5, 0.0 (virgin), 2.4, 1.2 (set1), 1.8, 0.9 (set2), 12.5, 5.1 (set3), and 6.1, 2.1 (set4), respectively. It should be noted that the contact angle of modified PVDF was affected by grafting degree as well as oxygen and sulfur content. The XPS analysis data support these results. This implies that grafting by electron beam irradiation and functional group conversion of epoxy to sulfonate is a key factor to decrease the hydrophobicity of PVDF.
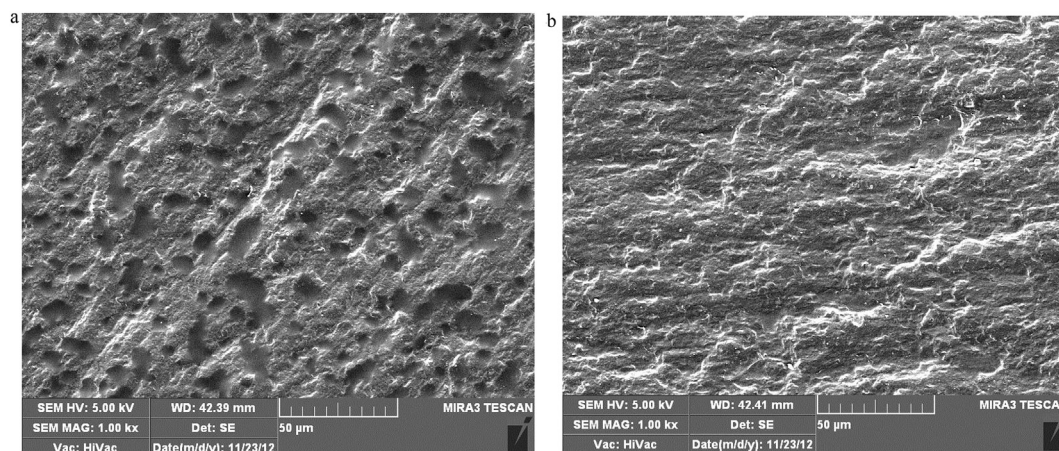

Fig. 4. SEM images of PVDF membranes (a) virgin (b) modified PVDF (test set 4).
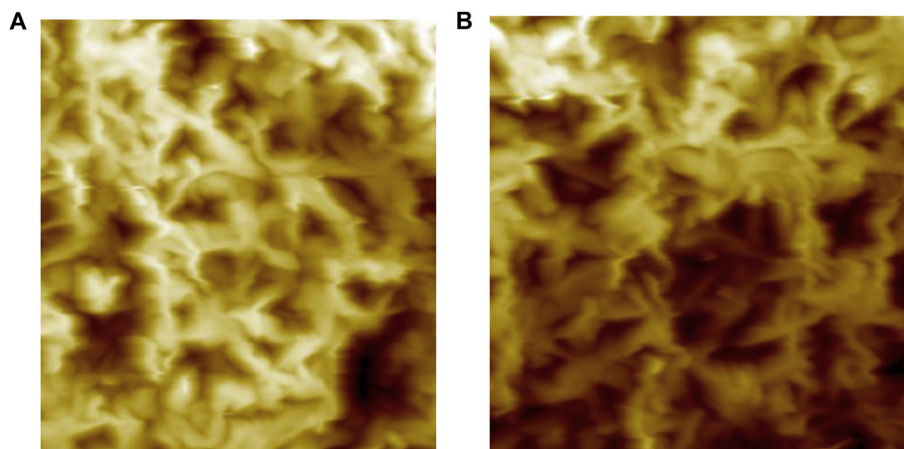
Fig. 5. Surface AFM images of PVDF (a) virgin (b) modified PVDF (test set 4).

Table 3
Roughness parameters obtained from AFM images of each test set.

Test set	GMA (w/w%)	EDMA (w/w%)	Ra (nm)	Rq (nm)
Virgin	0.0	0.00	527.2	639.9
Set 1	0.1	0.00	227.2	264.4
Set 2	0.1	0.02	140.1	186.3
Set 3	0.5	0.00	205.2	239.9
Set 4	0.5	0.10	138.6	181.1

Table 4
Comparison of ion exchange capacity between virgin and modified PVDF.

Test set	Ion exchange capacity (meq/g)
Virgin	0.00
Set 1	0.49
Set 2	0.44
Set 3	1.61
Set 4	1.55

Table 5
Variation of contact angle with grafting degree and oxygen and sulfur content.

Test set	Contact angle (degree)	Grafting degree (%)	Atomic ratio	
			O/C	S/C
Virgin	142	0.0	0.5	0.0
Set 1	110	0.7	2.4	1.2
Set 2	117	0.6	1.8	0.9
Set 3	48	3.5	12.5	5.1
Set 4	60	3.1	6.1	2.1

3.7. Water permeability

The water permeability of modified PVDF membranes was performed for 270 min busing a dead-end flux test system. The water permeability of each test set to treat domestic wastewater is shown in Fig. 6. The average permeability of each test unit was 17.9, 35.8, 59.4, 152.0, and 190.4 LMH/MPa corresponded to virgin, set1, set2, set3, and set4, respectively. The higher flux and longer filtration was maintained with the monomer concentration. Charged membranes provided the higher water permeability mainly due to their electrostatic repulsion and size exclusion. Negatively charged surface of colloidal solids and microorganism plays an important role in determining electrostatic repulsion between membrane and foulants, reducing the membrane fouling. This indicated that the enhanced hydrophilicity of PVDF influenced on water flux as well as membrane fouling. Although the addition of EDMA gave rise to the decrease of conversion degree and IEC, the higher flux and longer filtration was observed in this study. Masuelli et al. [33] reported that the radiation-induced graft polymerization generated denser and smaller pores, but the highest porosity was measured with the addition of crosslinker. This showed that hydrophilicity and morphology characteristics of modified membrane severely affect the filtration performance. The membrane was washed with pure water when the flux was severely depressed. The water permeability was almost completely recovered after cleaning procedure. The average recovered permeability was 15.6, 30.4, 50.5, 130.6, and 173.9 LMH/MPa corresponded to virgin, set1, set2, set3, and set4, respectively. 82.1–91.4% of flux was recovered by physical washing only. The rejection of organic matter and microorganism in domestic wastewater is shown in Table 6. The enhanced rejection of 12.8–19.7% for each test set was observed. The highest COD rejection was obtained at set 4 mainly due to its higher IEC and denser pore. On the other hand, solids and microorganisms were completely rejected irrespective of the radiation-induced graft polymerization.

4. Conclusions

The radiation-induced graft polymerization of PVDF was successfully carried out by electron beam irradiation. Glycidyl methacrylate and ethylenglycol dimethacrylate were used as monomers. Subsequently, oxirane groups of dehydrofluorinated PVDF was converted with sulfonic functional groups. The appearance of S2p3 peak in XPS analysis accompanied grafting and sulfonation by the contact angle decrease. The pore of grafted membrane was changed to elliptical and edgeless, and the roughness decreased with the monomer concentration.

Conflict of interest

The authors declare that there are no conflicts of interest including any financial, personal, or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.
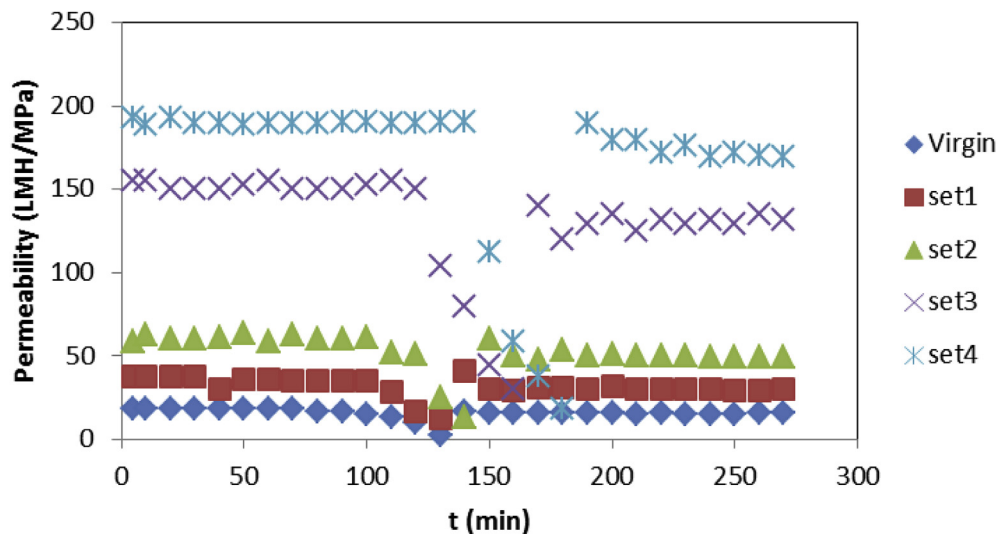
Fig. 6. Water permeability of each test set to treat domestic wastewater.

Table 6
Comparison of ion exchange capacity between virgin and modified PVDF.

Parameter	Permeate		
	COD (mg/L)	SS (mg/L)	Total coliform (CFU/100 mL)
Virgin	120.1	0	0
Set 1	71.4	0	0
Set 2	66.1	0	0
Set 3	49.4	0	0
Set 4	45.2	0	0

Acknowledgements

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