

Surface modification of polyvinyl chloride by polyacrylic acid graft as a polyelectrolyte membrane using Ar plasma

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Abstract: This work reports the synthesis and properties of a new membrane based on polyvinyl chloride (PVC) grafting with polyacrylic acid (PAA) using argon (Ar) plasma. The membranes of PVC were synthesized by solution-casting method, where PAA was deposited as an ultrathin film onto PVC using dielectric barrier discharge at atmospheric pressure with Ar gas. The surface characteristics and chemical composition of the modified membranes were analyzed by water contact angle, scanning electron microscopy, and Fourier transform infrared spectroscopy. Moreover, the electrochemical properties of the membrane were investigated via ion exchange capacity for the purpose of using it as a polyelectrolyte membrane.

Key words: Atmospheric plasma, electrolyte membrane, grafting polymerization, polyacrylic acid, polyvinyl chloride

1. Introduction

Fuel cells have advantages that have made them the first source of portable energy used in vehicles and simple buildings as an alternative to rechargeable batteries [1,2]. Therefore, polyelectrolyte membrane fuel cells (PEMFCs) are highly attractive due to their zero pollution emissions, simple procedure, high efficiency in energy conversion, and applied temperature suitable for residential and transportation applications. An important application of fuel cell systems in proton exchange membranes was the new generation of vehicles with PEMFCs in 1993 in the United States [3]. As is known, the polyelectrolyte membrane (PEM) is the most important part of the fuel cells. Thus, efforts have been made to achieve and develop techniques for preparing new or modified PEMs [4].

Plasma has many benefits and it represents an advanced technique in PEM technology [5–13]. Inert plasma gases such as He, Ar, and N₂ are commonly used to improve the characteristics of surfaces [14–18]. Meanwhile, plasma technology in atmospheric pressure has many advantages; low cost is one of its most important features [19]. Moreover, dielectric barrier discharge (DBD) is a good example of one of the best types of plasma active in atmospheric conditions [20]. It is a heterozygous secretion and needs little energy and alternating voltage. The chemical effects of plasma on the surfaces of hydrocarbons include crosslinking for thermal stability, etching to increase surface area, branching (grafting), and functionalization (hydrophilicity)

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[21–23]. The range of plasma effects depends on various parameters such as treatment time, discharge current power, and the working gas. The following are some examples of grafting processes using different plasma techniques.

The grafting of acrylic acid (AA) onto granular maize starch in aqueous medium initiated by ceric ions was studied gravimetrically under nitrogen atmosphere. Hydrogels were prepared by grafting AA onto gelatinized starch followed by neutralization with NaOH. The maximum obtained water absorption was 250 g/g [24].

AA was grafted to cellulose by using ceric ammonium nitrate (CAN) as an initiator in aqueous nitric acid solution at 30, 50, 70, and 90 °C with reaction periods from 30 to 180 min. Monomer conversion increased as reaction temperature increased and grafting yield decreased as reaction temperature decreased. Further study aimed to justify that high temperatures favor homopolymerization more than grafting [25].

Additionally, chitosan was grafted by AA using ceric ions as an initiator in the presence of N,N'-methylenebisacrylamide (MBA) as a cross-linker under microwave irradiation. The influences of microwave power and the amounts of initiator and cross-linker on the reaction were studied. The results showed that the microwave irradiation method can increase the reaction rate by eight times compared to the conventional method. The graft copolymer is an effective superabsorbent resin and can absorb 704 times more water than its relevant dry resin [26].

Abu-Saied et al. reported that polyvinyl chloride (PVC) membrane was grafted with polyacrylic acid (PAA) using plasma air/O₂ gas and they observed that a strong polar membrane surface was generated equipped with -COOH groups. However, the weight loss of the modified membranes was much less than that of the blank sample [27]. The detailed mechanisms of plasma treatments are still not fully understood [28, 29].

The grafting of PVC with hydrocarbon bearing a functional group (OH, COOH, etc.) allows varying the density of functional groups. The important part in the structure of PAA is the carboxylic groups. The carboxylic functions are not only able to promote a large amount of chemical reactions with different biomolecules (enzymes, antibodies, DNA, etc.) but also proton permeability. Therefore, carboxylic materials are sensitive to pH changes of the solution, so they are used in drug delivery systems. On the other hand, the halogen on the PVC membrane can be substituted easily with another functional group to improve the properties of such membranes.

In this work, the grafting of PVC membrane with PAA to improve the characteristics of fuel cell applications is reported. The thermal stability of the modified membranes is evaluated in comparison to blank PVC by thermogravimetric analysis, along with wettability and water uptake. The influence of amination with primary amine followed by sulfonation with respect to electrolytic properties is also explored. In this work, the acrylic is polymerized and joined to the PVC membrane in one step. Moreover, amination and sulfonation processes are done after grafting to improve the electronegativity of the PVC surface, which may accelerate the attraction of protons in the fuel cells.

2. Results and discussion

2.1. Chemical composition of membranes

The Fourier transform infrared (FTIR) spectra obtained from N₂, O₂, and Ar plasma-treated PVC followed by grafting with PAA and that of the pure PVC membrane (blank) are compared in Figure 1. All the PVC-g-PAA membranes showed similar IR spectra.

The characteristic peaks of PVC were recorded at ~2940 and 2880 cm⁻¹ CH_(as and sym), 1425 cm⁻¹ (δ_{CH₂}), 1255 cm⁻¹ (δ_{CH}), 1198 cm⁻¹ 1090 (ν_{C-C}), and 645 cm⁻¹ (ν_{C-Cl}) [30]. The PAA spectrum

exhibits a broadened band due to the νOH stretching vibration of COOH in the range from 2400 to 3700 cm^{-1} , overlapped with $\nu\text{CH}_{(as\ and\ sym)}$. Meanwhile, the $\nu\text{C}=\text{O}$ vibration appeared at $\sim 1700\text{ cm}^{-1}$, which indicates a successful grafting process.

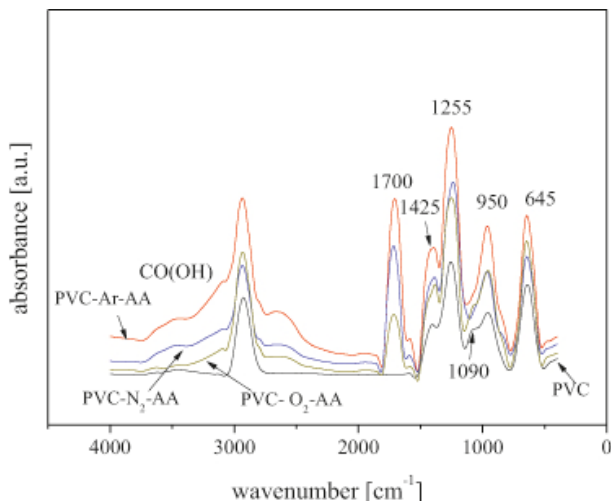


Figure 1. Spectra of ATR-IR of grafted PVC with PAA after treatments by different gases (O_2 , Ar , and N_2), compared to untreated PVC pure.

A procedure is employed to analyze the spectra quantitatively applying three Gaussians fitted to the data as shown in Figure 2a. One Gaussian is observed at $\sim 1669\text{ cm}^{-1}$ to describe the $\text{C}=\text{O}$ stretching modes of the hydrogen-bonded COOH group in the dimeric form (C_2O_4) [31]. The second contribution, associated with a shoulder at $\sim 1714\text{ cm}^{-1}$, is likely related to the vibration of the terminal group of oligomeric COOH chains, whereas the third component is located at 1756 cm^{-1} for the $\text{C}=\text{O}$ of the ester group. For all cases, the regression coefficient is better than 0.999. From the fitted areas of the Gaussians at 1714 cm^{-1} ($A_{\text{C}=\text{O}}$) and 945 cm^{-1} ($A_{\text{C}-\text{Cl}}$), the $A_{\text{C}=\text{O}}/A_{\text{C}-\text{Cl}}$ ratio is recorded for samples treated with different gases followed by grafting with AA as a measure of the COOH concentration.

The treatment of PVC membranes with Ar plasma could result in the generation of active sites on their surfaces, which in turn will attack the π bond in the AA monomer. Hence, covalent bonds are generated between the activated carbon on PVC and AA followed by the propagation process of AA and thereby a polymer layer was grafted onto the PVC. This may be confirmed by the broad band appearing in the region from 3600 to 2500 cm^{-1} and the band at 1700 cm^{-1} .

On the other hand, the PVC exposed to N_2 plasma has a comparatively marked effect as compared to the argon plasma-treated sample. However, in the case of O_2 plasma, in addition to the surface activation of the PVC membrane, functionalization of the polymer is predicted to occur because of the chemically active nature of O_2 gas (Figures 2a and 2b). This must lead to consumption of the active sites on the PVC surface [32], and therefore reduction of active sites and hindrance of the grafting process (Figure 2b). For that reason, Ar plasma was selected for the surface treatment in this study.

2.2. Wettability measurement

The contact angle of pure PVC membranes is reported in Figure 3 and compared to those modified with Ar DBD plasma and PVC-grafted AA in terms of surface water contact angle (WCA). The values of WCA decreased to lower than 20° in all cases of PVC-grafted AA membrane compared to that of the PVC blank at 54° . This

decrease in WCA values plausibly indicates the formation of hydrophilic layers (PAA) on the surface of PVC as discussed in the previous section, agreeing well with previous works [33].

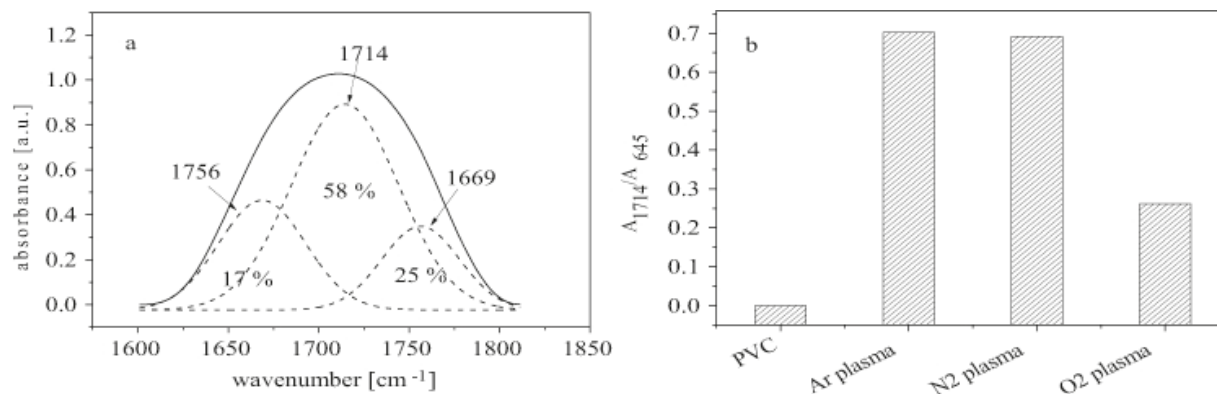


Figure 2. Stretching vibration of the carbonyl group ($C=O$) deconvoluted into three components (a) and the ratio of the COOH group in PAA as estimated by the 1714 cm^{-1} (A_{1714}) to 645 cm^{-1} (A_{645}) ratio with respect to different plasma gases (b).

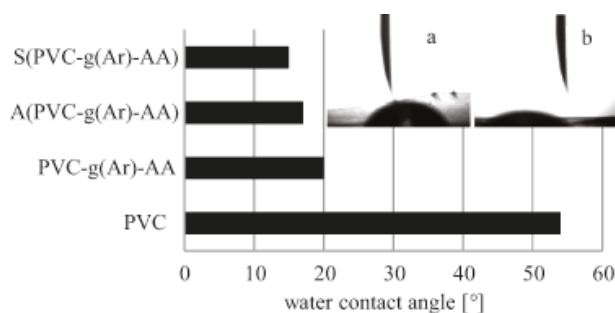


Figure 3. Contact angle of modified PVC with Ar gas compared to the untreated samples (PVC-g-AA), aminated A (PVC-g-AA), and sulfonated S (PVC-g-AA). The inset of Figure 3a represents a photograph of the contact angle between water and PVC, whereas 3b shows that between water and A (PVC-g-AA) as an example. A: Amination; S: sulfonation.

As is well known, Ar plasma introduces radicals and charges on the surface of hydrocarbons such as PVC membranes [34]. There are various methods and possibilities when such a modified membrane is immersed in an acrylic acid monomer. Initially, the charges and radicals on the surface act as an initiator for the polymerization process of AA (addition polymerization) [35]. Second, self-condensation of COOH groups in PAA may occur to produce ester groups [36]. Thus, a membrane with good wettability and adhesion is obtained. Hydrophilicity plays a key role in fuel cells, drug delivery, adhesion, bacterial behavior, and composite formation for polymer complexes.

In conclusion, the modified PVC membranes had better wetting features in comparison to the blank PVC, owing to the alteration of the chemical and morphological properties of the membrane surfaces after the grafting process. Moreover, the hydrophilicity of the membranes was improved by amination with polyethyleneimine followed by sulfonation processes because of the high electronegativity of the relevant groups [37–39].

2.3. Uptake (swelling degree)

The wettability in polymer electrolyte membranes is one of the advantages for proton transfer [40]. The swelling measurements were done at room temperature in deionized water, methanol, and ethanol. Additionally, the

swelling degree (uptake %) of aminated- and sulfonated PVC-g-PAA compared to pure PVC-g-PAA and the parent PVC membranes in water, methanol, and ethanol were recorded and are presented in Figure 4.

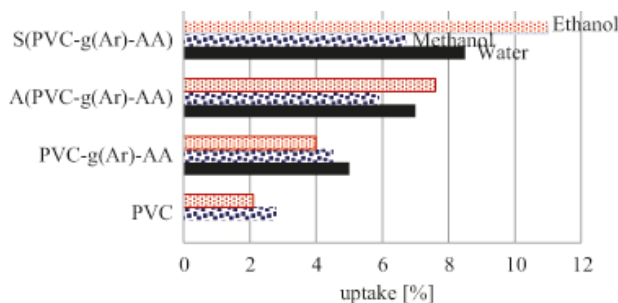


Figure 4. Water, methanol, and ethanol uptake % of PVC-g-AA, A (PVC-g-AA), and S (PVC-g-AA) and the untreated PVC membranes.

It is worth noting that the modification of PVC with Ar-plasma and then grafting through PAA has sharply affected the swelling degree of membranes. The resultant swelling data reveal that PAA acts as an electrolyte and therefore the water uptake % increased by deposition of PAA onto PVC membrane. Such an increase in water uptake obviously occurred following the amination process. Swelling degrees were also increased as a consequence of amination followed by sulfonation processes in water, methanol, and ethanol solvents. The introduction of sulfonic acid groups in the polymer chain induced a more hydrophilic performance to facilitate the conduction of protons [41].

The methanol uptake % results in comparison to other research (Table) indeed showed that the relevant values of the PVC membrane modified by Ar plasma followed by grafting with PAA are much better than those prepared from different molar ratios of PEC and PAA. These data confirm that the hydrophilicity of the PVC membrane is improved by grafting with PAA followed by amination and sulfonation.

Table. Comparison between the present work and another work in the case of methanol uptake as an example.

Membranes	Methanol uptake %	Ref.
PAA	0.08	[39]
PEC 25/75	0.63	
PEC 50/50	1.06	
PEC 60/40	1.2	
PEC 70/30	1.28	
PEC 80/20	1.29	
PEC 90/10	1.41	
PVC-g-AA (Ar plasma)	4.5	Current work
A (PVC-g-AA) (Ar plasma)	5.9	
S (PVC-g-AA) (Ar plasma)	6.7	

PEC = Polyelectrolyte chitosan.

2.4. Surface morphology

In aminated and sulfonated membranes no phase separation was observed; the changes in the structure because of the modified PVC membrane by subsequent amination and sulfonation processes have been proved. The conversion of the closed structure of PVC to an open pored structure because of the adjustment processes is also clear. The smooth surface morphology and glossy structure of the PVC-g-AA membrane (Figure 5) reveal homogeneity and the good matching between the two polymers' matrix components (i.e. PVC and PAA).

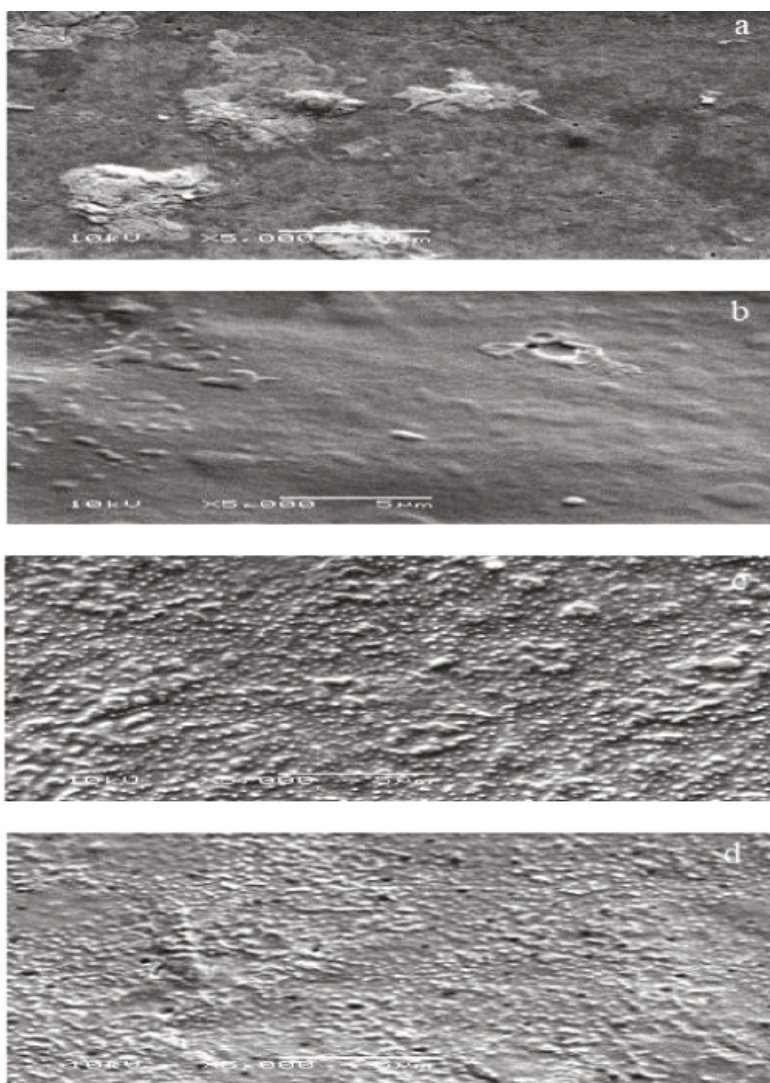


Figure 5. SEM pictures showing the surface morphology of PVC as a blank (a) compared to PVC-g-AA (b), aminated PVC-g-AA (c), and sulfonated PVC-g-AA membranes (d).

2.5. Ion exchange capacity (IEC)

The IEC values of pure PVC are very low, as expected due to the low level of ionized functional groups present in the membrane. On the contrary, the amination reaction progressed to create an appreciable IEC value, whereas inducing sulfonation offered better results than those of aminated ones (Figure 6).

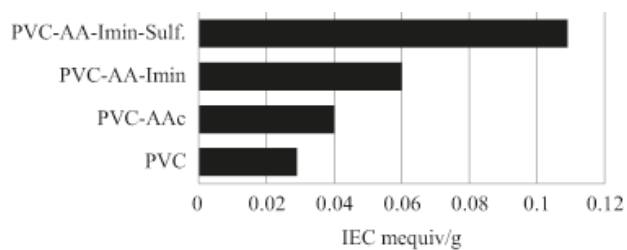


Figure 6. The change of IEC values in PVC-g-AA, A (PVC-g-AA), and S (PVC-g-AA) and blank PVC membrane.

The electronegativity of the membranes was enhanced by the amination process with imine due to the high electronegativity of amino groups. However, the sulfonic groups are more stable and have higher electronegativity values. This electronegativity can increase the proton permeability in such membranes and therefore it could be applied in direct methanol fuel cells.

2.6. Conclusion

Polyvinyl chloride was successfully cast as a membrane, modified by Ar plasma DBD at atmospheric pressure, and grafted with acrylic acid that was polymerized and deposited as an ultrathin film over the casting membranes of PVC. Two approaches were applied to modify plasma-induced surfaces. First, indirect modification by the interaction of noble Ar/He gases with the surface was applied, leading to generation of new free radical sites and thus reactive surfaces. Consequently, these brought reactive sites to bond with AA. Second, direct modification was applied by the interaction of either O₂ or CO₂ with the originating surfaces with OH/CO functional groups, therefore limiting the reaction with AA. The surface properties of modified membranes were changed to be more hydrophilic compared to the bulk. The electronegativity of the membrane surfaces was improved by amination and sulfonation processes. Therefore, the PVC-g-PAA membrane acted as an electrolyte membrane.

3. Experimental

3.1. Materials

PVC (3%) was from Sabic Company, H₂SO₄ and THF (99.5%) were from Fisher Chemicals Company, and polyethylene imine was from Acros. Acrylic acid, anhydrous (AAc, 99%) was from Sigma-Aldrich.

3.2. Membrane preparation

PVC membranes were prepared by casting a THF solution (3 wt./v%) in glass plates using a spreader knife to get dense membranes. Solvent evaporation was completed in 24 h at 60 °C. The thickness of membranes was measured and was in the range of 0.04 to 0.08 mm, whereas the thickness of the ultrathin layer of PAA that was grafted onto the PVC was ~2.5 nm [27].

3.2.1. Amination processes

The PVC-g-AA membrane was immersed in 10% polyethyleneimine at room temperature for 18 h and then washed with distilled water for 30 min and dried at 60 °C.

3.2.2. Sulfonation processes

Aminated PVC-g-AA membrane was rinsed in 4 M sulfuric acid at room temperature for 24 h, then washed again with distilled water for 30 min and dried at 60 °C.

3.3. Plasma system

DBD resembles the electrical discharge between two metal electrodes separated by an insulating dielectric material with high dielectric strength. A schematic diagram of the planar DBD system is shown in Figure 7. The discharge cell consists of two circular stainless-steel electrodes of 15 cm in diameter, separated by Pyrex glass sheet through an O ring leaving a gap space of about 1 mm.

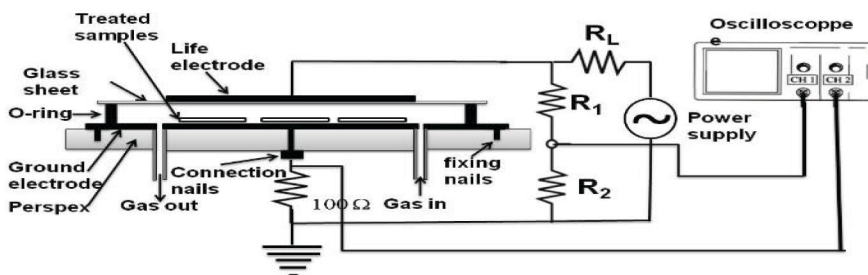


Figure 7. Schematic diagram of planar DBD.

The ground electrode is fixed on Perspex sheet with fixing nails connected to the ground through 100 ohm resistance. The outer electrode is connected to a high voltage AC transformer that generates a 50 Hz sinusoidal voltage (0–12 kV, 15 mA) used as an AC power source for driving the discharge. An inlet and outlet are connected to the ground electrode for gas insertion and exhaustion. A limiting resistor (R_L) is used to limit the discharge current, stabilize the discharge, and prevent formation of spark discharge. The polymer sample was put in the discharge gap between the two electrodes [42].

For this purpose, a plasma treatment process was conducted at a constant discharge power of 40 W. The current and voltage waveforms were recorded with a 100 MHz two-channel digital storage oscilloscope (type HM1508), where one channel was connected to a high voltage potential divider (1:1000) to measure the applied voltage on the discharge cell and the other channel was connected to 100 ohm resistance inserted between the inner electrode and the ground to measure the discharge current.

3.4. Instrumental and characterization methods

3.4.1. Contact angle

A contact angle meter (VCA 2500 XE) equipped with CCD camera and analysis software (AST Products, Billerica, MA, USA) was used to record the contact angle of water droplets with the prepared membrane as an indication of hydrophilicity. A droplet of water was placed on the surface of the polymer membrane and images were captured utilizing the attached camera [43].

3.4.2. Fourier transforms infrared spectroscopy (FTIR)

The chemical composition of the prepared membranes was analyzed via FTIR spectrometer (Shimadzu FTIR-8400s, Japan) in attenuated total reflectance (ATR) mode and scanned from wave number 400 cm^{-1} to 4000 cm^{-1} .

3.4.3. Surface morphology measurements

The morphological features and microstructures of the polymeric materials and their membranes were tested by SEM (JEOL JSM-6360LA, Japan).

3.4.4. Ion exchange capacity (IEC)

IEC is generally determined by volumetric method and it is directly dependent on the number of functional groups present in the polymer membrane. A membrane sample in the H^+ counterion form was drenched in 20 mL of 2 M NaCl solution at room temperature for 12 h.

The concentration of HCl freed from the membrane was titrated with a standard 0.1 N NaOH solution in the presence of phenolphthalein as an indicator. IEC was calculated as shown in Eq. (1) [44, 45]:

$$IEC = \frac{\text{Titer value (in mL)} \times \text{Normality of NaCl}}{\text{Wt. of dry polymer membrane (in g)}} \text{meq/g} \quad (1)$$

3.4.5. Solvent uptake

The water, methanol, and ethanol uptake of modified PVC and grafted ones in comparison to untreated membranes is usually defined in weight percent with respect to the weight of the dried membrane.

For measuring the swelling ability of PVC-g-PAA composite membranes, membrane samples were cut into 2 × 2 cm pieces and vacuum-dried for 12 h, and the dried sample weight was determined (W_{dry}). The dried membranes were rinsed in deionized water, methanol, and ethanol at room temperature, then weighed (W_{wet}) at specific interval times. The water uptake of the membranes was determined as in Eq. (2) [46]:

$$\text{Uptake (\%)} = [(W_{wet} - W_{dry})/W_{dry}] \times 100 \quad (2)$$

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