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## **POLYVINYL CHLORIDE MEMBRANES GRAFTING WITH POLYACRYLIC ACID VIA AR-PLASMA TREATMENT**

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### **ABSTRACT**

This work explores the synthesis and properties alteration of new composite membrane system 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 onto PVC using dielectric barrier discharge (DBD) at atmospheric pressure with different carrier gases such as (O<sub>2</sub>, Ar, N<sub>2</sub>, air) to get the optimum condition for grafting process of acrylic acid. Physicochemical properties were investigated as function of varied carrier gas for grafting process of PAA. ATR-FTIR has provided information on details of chemical structure of membrane, while morphological changes are characterized by scanning electron microscope (SEM). Moreover, mechanical properties of the membranes were studied using tensile strength (TS). Surprisingly, the wettability behavior of modified PVC membrane with AA vapor (plasma polymerization) is closed to such membranes those treated with O<sub>2</sub> plasma-AA liquid. An ultra-thin, pin hole free films of PAA were deposited onto PVC membranes leading to the increase of the wettability feature of the membranes. Meanwhile, ion exchange capacity (IEC) of such membranes was investigated by volumetric method and it is directly dependent on the electrochemical properties of membranes. The IEC values in case of grafting with PAA in vapor phase are promising and maybe related to the special structure of plasma deposited polymers. The grows in the electronegativity of the grafted and sulfonated membranes is an indication to the proton permeability. Therefore, such membranes may be used as polyelectrolyte membranes (PEM) in direct methanol fuel cell (DMFC).

**Key words:** polyacrylic acid, grafting, plasma treatment, polyvinyl chloride, fuel cells

### **1. INTRODUCTION**

A fuel cell is an electrochemical device that turns chemical energy stored in fuel into electrical energy, such as methanol, ethanol, formic acid and hydrogen, without combustion fuel cells are an alternative for high-price fossil fuels, as well as increased electricity dominance and higher greenhouse emissions. This energy, which is the fastest growing fuel cell, has some advantages such as high energy density and start-up time, low steering sensitivity and energy efficiency [1]. In 1993, the new generation of vehicles is one of the most important applications of fuel cell systems in the proton exchange membrane [2]. Fuel

cells are used as substitutes for rechargeable batteries, which are used as an important source of energy for buildings and vehicles because of their important advantages [3]. To make a modification or change in the surface of the polymer membrane, plasma technology is one of the most important ways for polyelectrolyte membranes (PEMs) [4, 5]. Because of the division and distribution of the surface of polymer membranes to a few nanometers, which earns good properties. A great effort has been made to develop and modify PEMs to convert these requirements. It is known and common when treating surfaces of membranes using plasma inert gas such as Ar, N<sub>2</sub> or He

with view seconds an activated surface are obtained [6,7]. Plasma technology at atmospheric pressure has many advantages and most importantly low cost [8,9]. Dielectric barrier discharge (DBD) is important and one of the best types of plasma active in the case of atmospheric pressure [10]. It is a heterozygous secretion and needs alternating voltage and low energy. Acrylic acid (AA) is a very appropriate monomer for plasma processes. It is volatile, soluble in water and easily polymerized. In addition to, the ratio of molarity of (-COOH) of the entire body is high, which gives increased wettability of the substrate. There are many of researches focus on plasma -induced graft copolymerization, both in vapor phase [11, 12] and liquid acid [11] solution [11-13]. Polymerization of acrylic acid by plasma technology [14]. Some of these researches deal with modifications in membranes. In this work the effect of different gases of plasma such as (O<sub>2</sub>, N<sub>2</sub>, air and Ar) gas on the grafting process of PAA onto PVC and electrochemical properties of membranes was studied. Moreover, the modified PVC membrane by Ar-plasma was exposed to acrylic acid monomer in liquid and vapor phase, followed by amination then sulfonation processes to improve the electrochemical properties of the membranes.

## 2. EXPERIMENTAL

### 2.1. Materials

Acrylic acid anhydrous AA 99%, polyvinyl chloride (PVC) (3%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and tetra-hydrofuran (THF) (99.5%), and polyethyleneimine were obtained from Sigma-Aldrich chemicals company, Sabic company, Fisher Chemicals Company and Across for Chemicals Company, respectively.

### 2.2. Membrane preparation

PVC polymeric material was dissolved in THF (3 wt./v%) solution and such solution was casted in glass plates using a spreader knife to obtain dense membranes. Solvent evaporation was completed after 24 h at 60 °C. The thickness of the membranes was measured and is equal from 0.04 to 0.08 mm where the thickness of ultra-thin layer of PAA that was grafted onto PVC was ~ 2.5 nm. A density of 1 g. cm<sup>-3</sup> is assumed to calculate the film thickness of grafted layers, because the

densities of ultra-thin layers are difficult to measure. Therefore, the values of the thicknesses may have an error, but this error was constant for all the discussed cases and relative changes can be discussed.

#### 2.2.1 Amination process

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

#### 2.2.2 Sulfonation process

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

### 2.3. Plasma system

Dielectric-barrier discharge (DBD) resembles the electrical discharge between two metal electrodes separated by an insulating dielectric material with high dielectric strength. 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 1mm. The ground electrode is fixed on Perspex sheet through fixing nails connected to the ground through 100 ohm resistance. The outer electrode is connected to a high voltage AC transformer generates a 50 Hz sinusoidal voltage (0-12kV, 15 mA) used as an AC power source for driving the discharge. An inlet and outlet is connected to the ground electrode for gas insertion and exhaustion. The current and voltage waveforms are recorded with 100 MHz two channel digital storage oscilloscope (Type HM1508, Taiwan) where one channel is connected to a high voltage potential divider (1:1000) to measure the applied voltage on the discharge cell, the other channel was connected to a 100 ohm resistance inserted between the inner electrode and the ground to measure the discharge current. For more detail see our previous work [15].

### 2.4. Instrumental characterizations

#### 2.4.1. Contact angle.

Contact angle meter VCA 2500 XE equipped with CCD camera and analysis

software (AST Products, Billerica, MA) were used to calculate the contact angle of water droplet with the prepared membrane as an indication for their hydrophilicity. Where, a droplet of water was laid onto the surface of polymer membrane and the images were hold utilizing the attached camera[16].

#### 2.4.2. Fourier transforms infrared spectroscopy (FTIR)

The chemical composition and interaction with (grafting) polymer of the prepared membranes were analyzed via Fourier transform infrared spectrometer (Shimadzu FTIR-8400s, Japan) in attenuated total reflectance (ATR) mode and scanned from the wave number of  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ .

#### 2.4.3. Tensile strength measurement

The morphological features and microstructure of the polymeric materials and their membranes were tested by SEM, JEOL JSM-6360LA, and Japan. Samples operated at an acceleration voltage of 20KV. Samples were pasted on stainless steel stubs with double tape followed by 10-20 nm thick layer of gold was sputtered on the samples by (JEOL.Ltd. Tokyo, Japan). Magnification power varied from 500-20,000.

#### 2.4.6. 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  $\text{H}^+$  counter ion form was drenched in 20 mL of 2 molar NaCl solution at room temperature for 12 h. The concentration of HCl freed from the membrane was titrated with a standard of 0.1N NaOH solution in presence of phenolphthalein. IEC in mills equivalents of functional groups per gram of dry sample was calculated as shown in Eq. (1)[17]:

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

#### 2.9. The uptake

(The water, methanol and ethanol uptake of the modified PVC and grafted one in

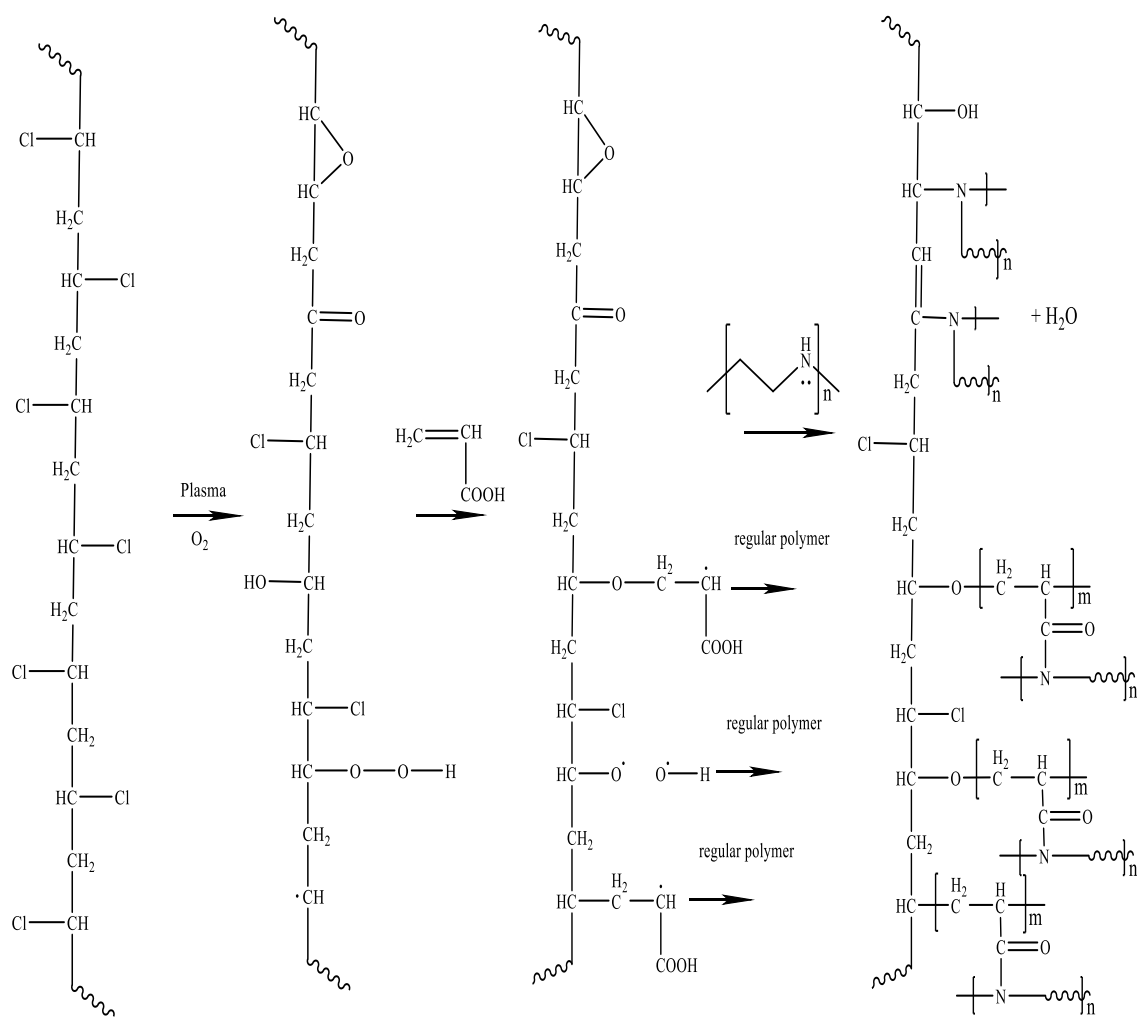
comparison to the untreated membranes is usually defined in weight percent with respect to the weight of the dried membrane. For measuring the swelling ability of PVC-g-PAA composite membranes, membrane samples were cut into  $2\text{ cm} \times 2\text{ cm}$  pieces and vacuum-dried for 12 h, the dried sample weight is determined ( $W_{\text{dry}}$ ). The dried membranes were immersed in deionized water, methanol and ethanol at room temperature, then weighted ( $W_{\text{wet}}$ ) at specific interval times. The water uptake of membranes was given as [18]: uptake (%) =  $[(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$ .

### 3. RESULTS AND DISCUSSION

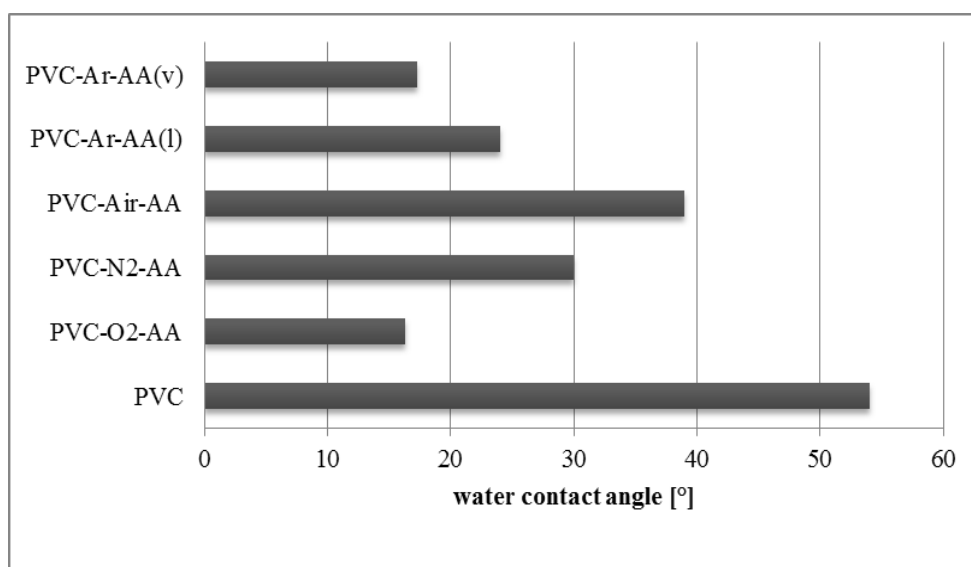
#### 3.2 Contact angle

Figure 1 reveals the contact angle values of pure PVC membranes and compared to those modified with different gases by DBD plasma treatment and grafted by acrylic acid (AA) in terms of surface water contact angle (WCA).

Results showed that, the values of WCA decreased from the original PVC blank value of  $54^\circ$  to  $16.3^\circ$  in case of PVC-g ( $\text{O}_2$ )-AA<sub>(l)</sub>,  $17.3^\circ$  for PVC-g (Ar)-AA<sub>(v)</sub>,  $24^\circ$  for PVC-g (Ar)-AA<sub>(l)</sub>,  $30^\circ$  for PVC-g ( $\text{N}_2$ )-AA<sub>(l)</sub> and  $39^\circ$  for PVC-g (air)-AA<sub>(l)</sub> membranes. It could be noted that WCA value in case of  $\text{O}_2$ -plasma and Ar-plasma with AA in vapor or liquid phase are closed and they lower than such values in case of  $\text{N}_2$  and air-plasma indicating to the hydrophilicity properties. This hydrophilic feature is an indication of incorporation of O groups (hydrophilic) on the surface and will detected using FTIR in the next section. Scheme 1 reveals the occurring chemical and theoretical reactions: An O – O bond (peroxide) would be created. However, this bond is not stable and no permanent chemical connection between the two materials is formed, therefore, a rearrangement of atoms was occurred leading to produce a new hydroxyl groups or maybe this molecule can connect the two polymers. It is therefore, named adhesion promoter. The hydroxyl groups on the surface can react with other chemical groups on the surface of a second material resulting in a covalent bond between the two materials.



**Scheme 1.** Suggested chemical effect of  $O_2$  plasma, grafting and amination processes on the PVC membrane.



**Fig. 1** Contact angle of modified PVC with different plasma gases ( $O_2$ ,  $N_2$ , air and Ar) compared to the untreated sample of PVC membrane.

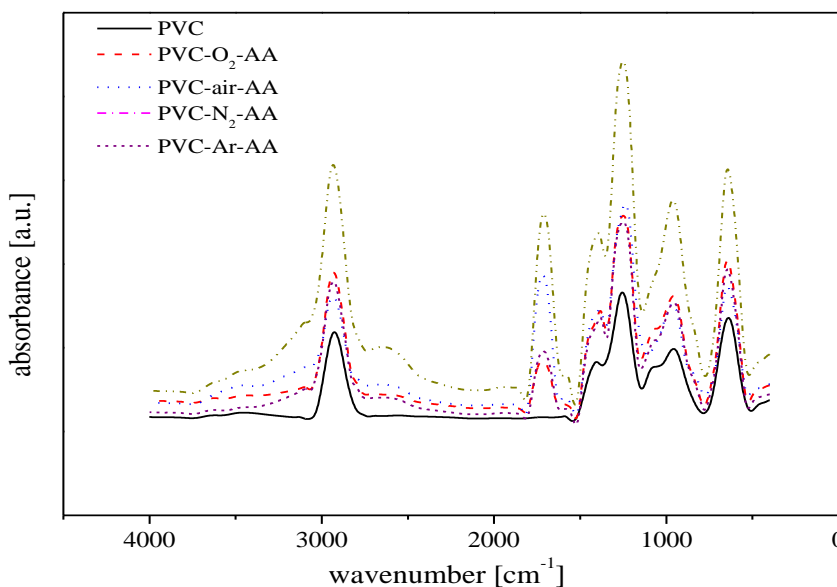
As discussed before,  $O_2$  plasma is considered as a good way not only to introduce the O groups such as OH, C-O-C, C=O, COOH, etc., but also radicals and charges can be formed during the plasma treatments on the surface of the hydrocarbon (PVC membrane). Therefore, there are different ways and possibilities when such modified membrane exposed to acrylic acid liquid or vapor monomer. First, such charges and radicals on the surface of membranes act as an initiator and react with the  $\pi$ -bond in AAc monomer followed by propagation and termination processes (addition polymerization)[19]. Thus, a covalent bonding of the deposited molecules to the substrate by radical – radical recombination was expected[20] and as will the stability of such grafted films in solvents. It is worth to be mentioned the hydrophilicity plays a key role in adhesion, drug delivery, fuel cells, composite formation or polymer-complexes and bacteria behavior. Further, the modified PVC membrane produce better wetting features in comparison to the blank PVC attributing to the change of the chemical and morphological properties on the surface of membranes after plasma treatment and grafting process. On the other hand, Ar as inert gas and  $N_2$  as semi-inert gas plasma are sources of radicals and active species on the surface of PVC[21]. Therefore,

the hydrophilicity of the surface of PVC was improved by Ar and  $N_2$  plasma treatments followed by grafting with AAc liquid monomer. Wherein, the grafting process was occurred on such active sites (radicals). However, the surface of PVC membrane was not covered completely by the active sites, therefore, the values of WCA are high in comparison to  $O_2$  plasma as discussed before. Surprising, the wettability behavior of PVC membrane after Ar plasma treatment with AAc vapor (plasma polymerization) is closed to the membrane treated with  $O_2$  plasma-AA<sub>(l)</sub>. In case of AAc vapor, plasma deposited polyacrylic acid PAA thin films were formed on the topmost surface layer of PVC membrane and Ar gas acts as a carrier gas. Thus, the ultra-thin, pin hole free films of PAA were deposited leading to the increase of the wettability feature of the membranes[22].

### 3.2. Chemical composition

FTIR spectra obtained from  $O_2$ ,  $N_2$ , Ar gases and air plasma-treated PVC followed by grafting with AA compared to pure PVC membrane (as blank) and presented in Figure 2. The observation: the PVC-g-PAA membranes showed similar IR spectra in all cases.

The characteristic peaks of PVC were taped at  $\sim 2940$  and  $2880\text{ cm}^{-1}$   $CH_{(as\ and\ sym)}$ ,  $1425\text{ cm}^{-1}$



**Fig. 2 Spectra of ATR-IR of the modified PVC with different gases such as  $O_2$ , Ar,  $N_2$  gases and air) followed by grafting with AA and compared to the untreated PVC.**

( $\delta_{\text{CH}_2}$ ),  $1255\text{ cm}^{-1}$  ( $\delta_{\text{CH}}$ ),  $1198\text{ cm}^{-1}$   $1090\text{ cm}^{-1}$  ( $\nu_{\text{C-C}}$ ),  $645\text{ cm}^{-1}$  ( $\nu_{\text{C-Cl}}$ ). The PAA spectrum exhibits a broaden band due to the inter- and intra-hydrogen bond corresponding to the  $\nu_{\text{OH}}$  stretching vibration of COOH in the range from  $2400$  to  $3700\text{ cm}^{-1}$ , overlapped with  $\nu_{\text{CH}}$  (as and sym).

Temporarily, the  $\nu_{\text{C=O}}$  vibration appeared at  $\sim 1700\text{ cm}^{-1}$  which indicates the successful grafting process. The treatment of PVC membranes with Ar plasma results in the generation of active sites on their surfaces, which in turn attack the  $\pi$ -bond in the AAC monomer. Hence, covalent bonds are generated between the activated carbon on PVC and AAC followed by the propagation process of AAC, thereby a polymer layer was grafted onto the PVC. This explanation might be confirmed by the broad band appearing in the region from  $3600$  to  $2500\text{ cm}^{-1}$  and the band at  $1700\text{ cm}^{-1}$  [23].

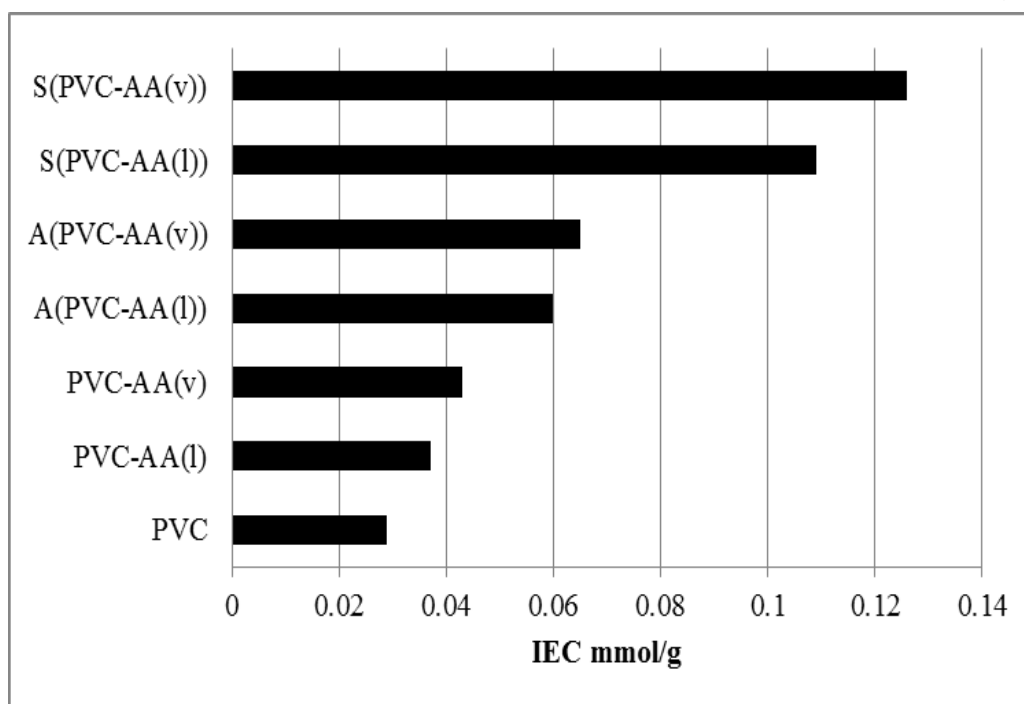
### 3.4. Tensile strength (TS)

The tensile properties of PVC pure and PVC-g-AAc (air plasma), PVC-g-AAc ( $\text{N}_2$  plasma) and PVC-g-AAc (Ar plasma) were measured and recorded. It was determined from

the critical breaking point of the stretching test pieces. The effect of force on the elongation of the membrane was observed as positive result where the elongation of the membrane is increased as a result of plasma treatment sample. The interesting observation is the tensile and elongation characters are the same behavior for all modified membranes. This may be explaining the improvement in the elongation and TS characters of the grafted membranes. It is worthy to mention pure PVC membranes have  $6.09\text{ (N)}$ , compared to PVC-g-AAc (Air plasma)  $5.1\text{ (N)}$ , PVC-g-AAc ( $\text{N}_2$  plasma)  $2.96\text{ (N)}$  and PVC-g-AAc<sub>(s)</sub> (Ar plasma)  $1.09\text{ (N)}$ . However, in case of vapor acrylic acid PVC-g-AAc<sub>(v)</sub> the max. force is  $8.9\text{ N}$ , where (l) indicate to AAC in liquid phase, (v) AAC in vapor phase. As discussed before, an ultra-thin cross-linked and pin hole free film of PAA was deposited onto PVC membrane leading to improve the mechanical properties of the membranes.

### 3.5. Ion exchange capacity (IEC)

On the contrary, the amination reaction is progressed to create an appreciable IEC value, whereas inducing sulfonation offer better results than those of aminated ones (Figure 3).



**Fig. 3** The IEC values of PVC-AA(l), PVC-AA(v), A(PVC-AA(l)), A(PVC-AA(v)), S(PVC-AA(l)), S(PVC-AA(v)) in comparison to the PVC blank membrane. Where (l) = grafting in liquid phase, (v) = grafting in vapor phase, A: aminated and S: sulfonated.

The electronegativity of the membranes was improved by amination process with imine due to the high electronegativity of amino groups. However, the sulfonic groups are more stable and higher in electronegativity values. This electronegativity can accelerate the proton permeability in such membrane and therefore, it could be applied in direct methanol fuel cells. Moreover, the IEC values in case of grafting with PAA in vapor phase are the best corresponding to the special structure of plasma deposited polymers.

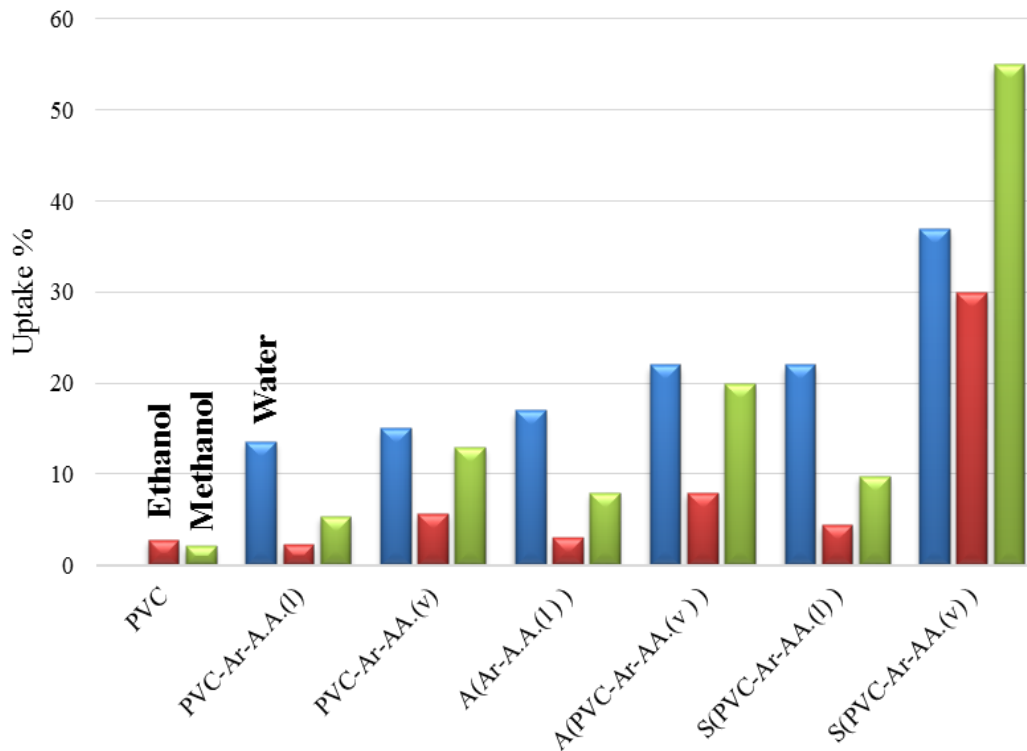
### 3.6. The uptake

The wettability in polymer electrolyte membrane is one of the advantages for proton transfer. The swelling degree (uptake %) of PVC-PAA-imine compared to PVC membranes were shown in Fig. 4. The swelling measurements were done at room temperature in deionized water, methanol and ethanol. It is worth noting that, the modified PVC by Ar-plasma then grafted with PAA has affected sharply on the swelling degree of membranes.

The resultant swelling data refers that, PAA acts as an electrolyte and therefore, the water uptake % increased by deposition of PAA onto PVC membrane and this increase was obviously after amination process. Besides the swelling degrees was increased with amination followed by sulfonation process in water, methanol and ethanol solvent [24].

### CONCLUSION

PVC was successfully casted as membrane and modified by Ar plasma followed by grafting with ultra-thin film of polyacrylic acid. Dielectric barrier discharge in atmospheric pressure is a good and cheap way to graft the PVC membrane with acrylic acid in liquid or even vapor phase. A hydrophilic surface of modified PVC membrane was obtained. Such modified membrane maybe acts as an electrolyte membrane specially after grafting process with acrylic acid vapor followed by sulfonation process indicating by the increase of the water uptake values of membranes.



**Fig. 4** Water, methanol and ethanol uptake % of PVC-AA(l), PVC-AA(v), A(PVC-AA(l)), A(PVC-AA(v)), S(PVC-AA(l)) and S(PVC-AA(v)) compared to the untreated PVC membranes.

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### الملخص العربي :

هذا العمل يهدف الي تحضير وتعديل لصفات غشاء جديد من عديد كلوريد الفينيل وذلك عن طريق عمل تطعيم له بحامض الاكريليك باستخدام غاز الأرجون في حالة البلازما. تم تحضير غشاء عديد كلوريد الفينيل بطريقة صب المحلول ثم تم ترسيب عديد حامض الأكريليك علي سطح غشاء عديد كلوريد الفينيل باستخدام البلازما من النوع ثنائي الحاجز العازل في الضغط الجوي وتم استخدام أنواع مختلفة من الغازات مثل (الأرجون والأكسجين والنيتروجين والهواء ) وذلك بهدف الوصول إلي أفضل حالة تطعيم بحامض الأكريليك . تم عمل فحص للخواص الفيزيوكيميائية لعملية التطعيم بعديد حامض الأكريليك عند استخدام غازات مختلفة مثل (الأكسجين و الأرجون والنيتروجين والهواء ) . طيف الأشعة تحت الحمراء ATR-FTIR تم استخدامها بغرض اظهار التركيب الكيميائي للغشاء كما تم استخدام المجهر الإلكتروني الماسح لتفسير التغيرات المورفولوجية وتم دراسة الخواص الميكانيكية للأغشية باستخدام قوة الشد. ومن المثير للدهشة أن سلوك قابلية غشاء عديد كلوريد الفينيل للتبلل بعد عملية البلمرة ببلازما الأرجون وبتطعيم حامض الأكريليك في حالته البخارية قريبة من نتائج عملية البلمرة ببلازما الأكسجين والتطعيم بحامض الأكريليك في صورته السائلة . تم عمل ترسيب لطبقة رقيقة جدا من عديد حامض الأكريليك خالي من الثقوب علي سطح غشاء عديد كلوريد الفينيل مما زاد من عملية التبلل. وفي الوقت نفسه ، تم التحقيق في قدرة التبادل الأيوني (IEC) لهذه الأغشية بالطريقة الحجمية وهي تعتمد بشكل مباشر على الخواص الكهروكيميائية لهذه الأغشية. تعد قيم IEC في حالة التطعيم باستخدام PAA في الحالة البخارية واعدة وربما تتعلق بالتركيب الكيميائي للبوليمرات المرسبة بالبلازما. نمو السالينية الكهربائية للأغشية المطعمة وعملية السلفنة تعد إشارة إلى نفاذية البروتون. لذلك ، يمكن استخدام هذه الأغشية كأغشية متعددة الإلكترونات في خلية وقود الميثانول المباشرة.