

Preparation and Characterization of Novel Grafted Cellophane-Phosphoric Acid-Doped Membranes for Proton Exchange Membrane Fuel-Cell Applications

M. A. Abu-Saied,^{1,2} A. A. Elzatahry,^{1,2} K. M. El-Khatib,³ E. A. Hassan,⁴ M. M. El-Sabbah,⁴ E. Drioli,^{5,6} M. S. Mohy Eldin¹

¹Polymer Materials Research Department, Advanced Technologies and New Materials Research Institute (ATNMRI), Mubarak City for Scientific Research and Technology Applications (MUCSAT), New Borg El-Arab City, Alexandria 21934, Egypt

²Chair of Petrochemicals, Department of Chemistry, Faculty of Science, King Saud University, Riyadh, KSA

³Pilot Plant Department, Engineering Division, National Research Center, Dokki, Giza, Egypt

⁴Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt

⁵National Research Council—Institute for Membrane Technology (ITM-CNR), Via Pietro BUCCI, c/o The University of Calabria, Cubo 17/C, 87030 Rende CS, Italy

⁶Department of Chemical Engineering and Materials, The University of Calabria, Cubo 44/A, Via Pietro BUCCI, 87030 Rende CS, Italy

Received 16 April 2011; accepted 8 June 2011

DOI 10.1002/app.35048

Published online 22 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This work concerns preparation of acid-base polyelectrolyte membranes for fuel-cell applications from cellulosic backbones for the first time. Grafted cellophane-phosphoric acid-doped membranes for direct oxidation methanol fuel cells (DMFC) were prepared following three steps. The first two steps were conducted to have the basic polymers. The first step was introducing of epoxy groups to its chemical structure through grafting process with poly-(glycidylmethacrylate) (PGMA). The second step was converting the introduced epoxy groups to imides groups followed by phosphoric acid ($-\text{PO}_3\text{H}$) doping as the last step. This step significantly contributes to induce ion exchange capacity (IEC) and ionic conductivity (IC). Chemical changes of the cellophane composition and morphology characters were followed using FTIR, TGA, and SEM analysis. Different factors affecting the membranes characters especially IEC, methanol permeability, and thermal stability

were investigated and optimized to have the best preparation conditions. Compared to Nafion 117 membrane, cellophane-modified membranes show a better IEC, less methanol permeability, and better mechanical and thermal stability. IEC in the range of 1–2.3 meq/g compared to 0.9 meq/g per Nafion was obtained, and methanol permeability has been reduced by one-order magnitude. However, the maximum obtained IC for cellophane-PGMA-grafted membrane doped with phosphoric acid was found 2.33×10^{-3} (S cm^{-1}) compared to 3.88×10^{-2} (S cm^{-1}) for Nafion 117. The obtained results are very promising for conducting further investigations taking into consideration the very low price of cellophane compared to Nafion. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3710–3724, 2012

Key words: grafted polymer; fuel cell; polymer electrolyte membrane; modified cellophane

INTRODUCTION

The direct methanol fuel cell (DMFC) is attracting much interest as an energy source for transport and other portable applications. Commercialization of the DMFC is at present inhibited by two major technical problems. The first problem is the low performance of DMFCs due to the slow kinetics of the oxidation reaction of methanol at the anode. The second problem is methanol diffusion from the anode to the cathode side of the DMFC, through the poly-

mer electrolyte membrane. This methanol permeability causes conversion losses in terms of lost fuel and depolarization losses at the cathode, resulting in overall poor fuel-cell performance.¹

The per fluorinated sulfonic acid membrane Nafion[®] is commonly used as electrolytes in DMFCs, owing to their good chemical and thermal resistance and ionic conductivity (IC). However, it has been found out that over 40% of the methanol can be wasted in DMFCs through leaks across such membranes.² To overcome these problems, two major approaches have been proposed. The first approach is to enhance the oxidative methanol reaction kinetics on the anode. Certainly, an improvement in the efficiency of the catalyst can drastically improve the kinetics of the methanol oxidation reaction and increase the chances of commercialization of the

Correspondence to: Dr. M. S. Mohy Eldin (mohyeldinmohamed@yahoo.com).

DMFCs. The second approach is to use membranes possessing inherent characteristics of high proton conductivity along with low methanol permeability. It is believed that remarkable improvements in energy efficiency and cell voltage would result from improved methanol anode kinetics and a drastic reduction or stop of methanol crossover.

It is the second approach that will be focused on in this study; to synthesize and evaluate the methanol permeability of an alternative membrane for DMFC application. The most serious problem that hinders efforts to commercialize profitable DMFC is the high cost, which must be overcome as soon as possible.

Acid-base complexation represents an effective approach to the development of proton-conducting membranes.³ Basic polymers can be doped with an amphoteric acid, which acts both as a donor and an acceptor in proton transfer and therefore allows for the proton migration. H₃PO₄-doped PBI has received much attention in the past few years.^{4,5}

Another type of acid-base polymer membranes was developed by Kerres' group.⁶ In their efforts to reduce polymer swelling, they found that the base protonation and hydrogen bridging in acid-base blend membranes markedly reduce the swelling. The resulting acid-base blends constitute a new class of proton-conducting membranes with high conductivity, thermal stability, and mechanical flexibility and strength.

Polymers bearing basic sites such as ether, alcohol, imine, amide, or imide groups react with strong acids such as phosphoric acid or sulfuric acid. The basicity of polymers enables the establishment of hydrogen bonds with the acid. In other words, the basic polymers act as a solvent in which the acid undergoes to some extent dissociation.

Because of their unique proton conduction mechanism by self-ionization and self-dehydration,⁷ H₃PO₄ and H₂-SO₄ exhibit effective proton conductivity even in an anhydrous (100%) form. When a basic polymer is present, the interaction between these acids and the polymer through hydrogen bonding or protonation would increase the acid dissociation, compared to that of anhydrous acids.

A number of basic polymers have been investigated for preparing acid-base electrolytes, such as PEO,^{8,9} PVA,¹⁰ polyacrylamide,^{8,11–13} and polyethylenimine (PEI).¹⁴ Recently, Nylon¹⁵ and poly(diallyldimethylammonium-dihydrogen phosphate)¹⁶ have also been investigated. Most of these acid-polymer blends exhibit proton conductivity less than 10⁻³ S cm⁻¹ at room temperature. When plotted as a function of the acid content, the conductivity seems to have a minimum at the composition where the maximum protonation is reached.^{3,17} High acid contents result in high conductivity but sacrifice mechanical

stability, especially at temperatures above 100°C. Another concern is the oxidative stability of the tertiary C—H bonds in applications for fuel cells.

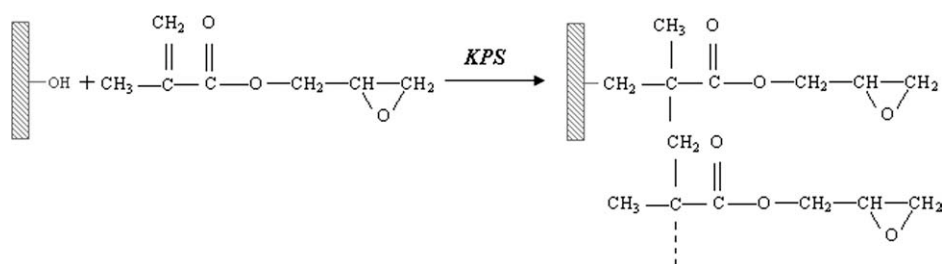
To improve the mechanical strength, efforts in this field have been made by (1) crosslinking of polymers (e.g., PEI¹⁴) (2); using high *T_g* polymers such as PBI and polyoxadiazole¹⁸; and (3) adding inorganic filler or/and plasticizer,¹⁹ as recently reviewed by Laségues et al.¹⁹ Phosphoric-acid-doped PBI has received the most attention. The combination of the acid and polymer forms a solid polycation at low acid contents. When the acid content is higher, the plastifying effect of the excessive acid sometimes leads to the formation of a soft paste, which is unable to be processed into membranes. Addition of an inorganic filler such as high-surface-area SiO₂ would make the materials stiffer, as demonstrated in systems of PEI-H₃PO₄-SiO₂,¹⁷ SiO₂-PVDF-acid,²⁰ and Nylon-H₃PO₄/H₂SO₄-SiO₂.¹⁹ The latter was reported to exhibit a room-temperature conductivity as high as 10⁻¹ S cm⁻¹.

Most of the studied acid/polymer systems are not entirely anhydrous, as water is present as a necessary plasticizer for improving conductivity and mechanical properties. Gel electrolytes, as often termed, are obtained by the introduction of organic plasticizers such as propylene carbonate (PC), dimethylformamide (DMF), and glycols.²¹ DMF²² and PC/DMF^{12,23} have also been used as plasticizers in H₃PO₄-PVDF and acid-PMMA systems.

Recently, crosslinked polymer electrolyte membranes based on cellulose and sulfosuccinic acid for fuel-cell applications were prepared through crosslinked reaction between —OH of cellulose and —COOH of sulfosuccinic acid via esterification.²⁴ No publications, up to the knowledge of the authors, have been dealt with the preparation of acid-base polymer membranes for fuel-cell applications starting from cellulose backbone.

In this article, novel acid-base polyelectrolyte membranes for fuel-cell applications have been prepared from cellulosic materials backbone for the first time.

Poly(glycidylmethacrylate) (PGMA)-grafted cellophane-phosphoric acid-doped polyelectrolyte membranes were prepared and characterized for prospective DMFC applications. To have the basic polymer, first, cellophane membranes were grafted with PGMA using persulphate initiation system and the effect of different polymerization conditions, such as monomer and initiator concentration, polymerization temperature, and time on the grafting process parameters was explored. Three parameters namely grafting percentage, grafting efficiency, and weight conversion were monitored. Second, the introduced epoxy groups of PGMA were subsequently converted into imide groups by amination process using



Scheme 1 Mechanism of cellophane grafting.

ethylene diamine (EDA). The amination conditions such as EDA concentration, reaction time, and temperature were investigated. Crosslinking action of EDA could be an additional action that helps in improving both mechanical and thermal properties of the prepared basic polymer membranes. Finally, the basic polymer membranes were doped with orthophosphoric acid (OPA), and the doping conditions, such as OPA concentration, reaction time, and temperature, were investigated to have the optimum conditions. In the part of membrane's characterization, different characters related to the final application were evaluated: namely water uptake, methanol uptake, dimensions changes, tensile strength (TS), membrane thickness changes, ion exchange capacity (IEC), methanol permeability measurements, and finally Membrane's IC. FTIR and TGA analysis provided proved for the occurrence of the grafting process while the homogeneity of the formed graft copolymer was examined by SEM analysis.

EXPERIMENTAL

Materials

- Glycidylmethacrylate (GMA) (purity 97%) is obtained from Sigma-Aldrich Chemicals, (Switzerland).
- Cellophane sheets were kindly supplied by Misr Rayon Co. Kafr El-Dawar (Egypt) type, uncoated; dimensions, 80 × 117 cm; cellulose content 80% (wt %); regenerated cellulose; additives content 20% (glycerol and Na₂SiO₃). The additive was removed by extraction with hot-distilled water and then the films were cut with dimensions 5 × 5 cm.
- Potassium persulphate (KPS) (purity 99%, M. wt. 270.31) Sigma-Aldrich Chemicals (Germany).
- Ethyl alcohol absolute (purity 99.9%) El-Nasr Pharmaceutical Co. for Chemicals. (Egypt).

- Sulfuric acid (purity 95–97%) Sigma-Aldrich Chemicals (Germany).
- Methanol (purity 99.8%) Sigma-Aldrich Chemicals (Germany).
- Orthophosphoric acid (purity 85% extra pure) Sigma-Aldrich Chemicals (Germany).
- Ethylenediamin (purity 99%) Loba Chemie (India).
- Hydrochloric acid (purity 30–34%) El-Nasr Pharmaceutical Co. for Chemicals (Egypt).
- Sodium chloride (purity 99.5%, M. wt. 58.44) Sigma-Aldrich Chemicals (Germany).

Methods

Membrane preparation

Grafting process. Cellophane membranes with 5 × 5 cm dimensions were soaked into GMA-ethanol/water monomer solution. Different monomer concentrations (8–20% v/v) were used with KPS initiator (0.004–0.012M). Grafting process was carried out in a water bath at different temperatures (35–65°C) for different time intervals (1–5 h) (Scheme 1). The grafting containers were left at R.T for 24 h after ending the grafting time to complete the postgrafting process. After completion of the grafting process, the grafted cellophane membranes were removed, and the physically adhered homopolymers were washed out using distilled water and collected to be dried in an air drier at 105°C for 24 h. The grafted membranes were then extracted with chloroform using Soxhlet to remove included homopolymers. The grafted membranes were then dried at 60°C in air drier over night and then weighted to calculate the grafting percentage (GP, %) as mentioned in eq. (1). To have complete characterization of the grafting process, other grafting parameters namely grafting efficiency (GE %) and weight conversion (WC %) were estimated using eqs. (2) and (3).²⁵

$$GP\% = \frac{\text{Wt of grafted membrane after ext} - \text{Wt of original membrane}}{\text{Wt of original membrane}} \times 100 \quad (1)$$

$$GE\% = \frac{\text{Wt of grafted membrane} - \text{Wt of original membrane}}{\text{Wt of grafted polymers} + \text{Wt of homopolymer}} \times 100 \quad (2)$$

$$WC\% = \frac{\text{Wt of grafted polymer} + \text{Wt of homopolymer}}{\text{Wt of used monomer}} \times 100 \quad (3)$$

Amination process. PGMA-grafted cellophane membranes with selected grafting percentage were reacted with EDA of different concentrations (1 : 6% v/v) in aqueous medium at different temperatures (25–65°C) for different time intervals; 2–10 h (Scheme 2). The epoxy groups of the PGMA chains accordingly were opened through reaction with primary amino groups of EDA. After completion of the amination process, the aminated PGMA-grafted membranes were washed with distilled water to remove excess of unreacted EDA.

Phosphoric acid-doping process. Aminated PGMA-grafted cellophane membranes were doped with phosphoric acid using OPA aqueous solution of dif-

ferent concentrations (1.5–7.5% v/v). The process was carried out at different temperatures (25–65°C) in a water bath for different time intervals (2–10 h). After ending the reaction time, the doped membranes were washed with distilled water to remove excess of unreacted OPA.

Membrane characterization

Water uptake (W_{H_2O} %). Membranes were immersed in distilled water at room temperature for 24 h and then their surfaces were dried by wiping with filter paper and weighing. The obtained results are the average of three samples.²⁶

$$W\% = \frac{\text{Wt of membrane (gm)} - \text{Wt of dry membrane (g)}}{\text{Wt of Dry membrane (gm)}} \times 100 \quad (4)$$

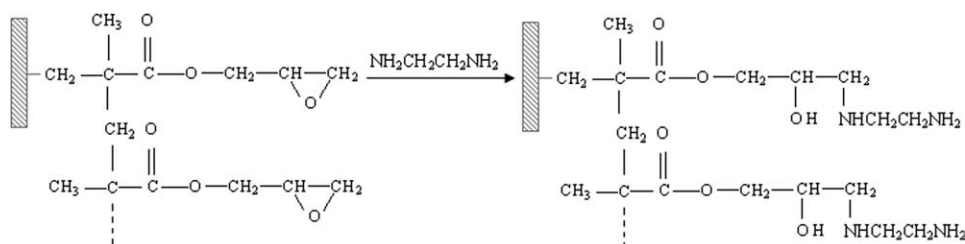
Methanol uptake (W_M %). Membranes were immersed in pure methanol at room temperature for 24 h and then their surfaces were dried by wiping

with filter paper and weighing. The obtained results are the average of three samples.²⁶

$$W\% = \frac{\text{Wt of membrane (gm)} - \text{Wt of dry membrane (g)}}{\text{Wt of Dry membrane (gm)}} \times 100 \quad (5)$$

Dimensional changes (Δa %). Changes in membranes dimensions were measured by immersing the membranes into deionized water or pure methanol at

room temperature for 24 h. The area change percentage ($\Delta A\%$) was calculated according to the following equation:



Scheme 2 Mechanism of amination of PGMA-g-cellophane membranes.

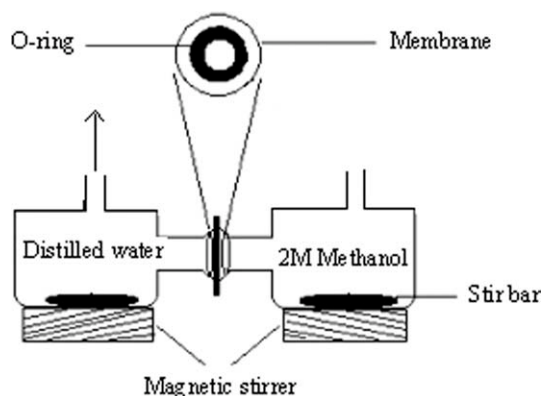


Figure 1 Glass diffusion cell for methanol permeability measurements.

$$\Delta A\% = \frac{A - A_0}{A_0} \times 100 \quad (6)$$

A_0 and a is the area of membrane before and after soaking treatment, respectively.

Infrared spectrophotometric analysis. Functional groups investigation in both ungrafted and modified membranes having different GPs was carried out using Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan).

Thermal gravimetric analysis. Thermal characterization for both ungrafted and modified membranes having different GPs was carried out using Thermogravimetric Analyzer (Shimadzu TGA-50, Japan).

Scanning electron microscopic analysis. Surface characterization of ungrafted and modified membranes was carried out using energy-dispersive analysis X-ray (Joel Jsm 6360LA, Japan).

Ion exchange capacity. The ion exchange capacity (IEC) of the phosphoric acid-doped membranes was determined using acid-base titration. Weighed samples were placed in 20 cm³ of a 2M NaCl solution for at least 12 h. The solution was then titrated with a NaOH solution of known concentration. IEC was calculated as follows:

$$IEC(\text{meq/g}) = n(\text{mmol/cm}^3) \times v(\text{cm}^3)/w(\text{gm}) \quad (7)$$

where n , v , and w are the concentration of the NaOH solution, the titer of the NaOH solution, and the weight of the sample, respectively.²⁷

Methanol permeability. Methanol permeability measurements were carried out using a home made, glass, and diffusion cell that consisted of two cylindrical glass compartments (A for feed and B for permeate) separated by a membrane. A schematic representation of the methanol diffusion cell is presented in Figure 1. Compartment A was filled with 15 wt % methanol ($V_A = 125$ mL) and compartment B with deionized water ($V_B = 120$ mL).

Both the feed and the permeate solutions were kept under continuous stirring conditions by magnetic stirrers. To determine the methanol permeability of each membrane, liquid samples of 100 μL were taken from the permeate using a syringe at prescribed time intervals. The liquid samples were analyzed with a calibrated gas chromatograph (GC-17 A, Shimadzu, Japan).

Methanol permeability calculation. The methanol permeability (P) was determined for each membrane sample as follows: methanol diffusion was established across the membrane due to a concentration gradient. The concentration of methanol in the permeate compartment is given by eq. (7), as stated elsewhere.²⁸

$$\frac{V_B dC_B}{dt} = A \times \frac{DK}{L} C_A \quad (8)$$

where C_B is the concentration of methanol in the permeate (water) compartment at time t , C_A the concentration of methanol in the feed compartment, A the membrane cross-sectional area, L the membrane thickness, V_B the volume of the water compartment, D the methanol diffusivity, and K is the partition coefficient. Equation (8) can be solved to give

$$C_B(t) = \frac{A}{V_B} \times \frac{DK}{L} C_A (t - t_0) \quad (9)$$

where t_0 is the time lag, which is explicitly related to the diffusivity ($t_0 = L^2/6D$). Because the permeability (P) is defined as the product of the diffusivity of methanol through the membrane (D) and the partition coefficient (K), that is, $P = DK$, eq. (9) can be rewritten as follows:

$$C_B(t) = \frac{A}{V_B} \times \frac{P}{L} C_A (t - t_0) \quad (10)$$

The methanol permeability (P) is calculated from the linear relationship of concentration change of C_B versus time (t) according to the following expression:

$$P = \alpha \times \frac{V_B}{A} \times \frac{L}{C_A} \quad (11)$$

where α is the slope of the linear plot of C_B versus t . **IC measurement.** Proton conductivity was measured via impedance spectroscopy using a impedance/gain phase analyzer Solartron 1260 (AC amplitude 100 mV; initial frequency 10 MHz and final frequency 10 Hz), and the results were elaborated by the Zplot software (Scribner Associates, USA).

The impedance data were corrected for the contribution of the empty and the short-circuit cell. Before

the test, the membranes (disc with $\phi = 9$ mm) were soaked in a 0.1M H_2SO_4 solution for 24 h and after in water for other 24 h and then dried on the surface before the measurements.

The samples were clamped between two carbon paper electrodes (E-TEK Elat, 1 mg/cm² Pt; 20 wt % Pt/VXC72) in a two compartment cell described in our previous works.²⁹

The operative conditions were temperature 46°C; relative humidity 98%.

The conductivity of the samples in the transverse direction was calculated from the impedance data, using the following relationship:

$$\sigma = \frac{d}{R \cdot S} \quad (12)$$

where σ is the conductivity (S cm⁻¹), d (cm) and S (cm²) are, respectively, the thickness and area of the sample, and R (Ω) is the membrane resistance. R was derived from the intercept at high frequency with real axis of the impedance in the Nyquist plot (imaginary component versus real component of the impedance).

TS measurement. Tensile strength (TS) is a measure of the resistance of sample to direct tension. It is defined as the force required breaking a strip of sample, which has a specified length and a width of 10 mm. LLOYD Instruments LR 10 K was used for TS measurements

- Breaking length (m) = TS (kg) \times length of strip (m)/weight of strip (kg).
- 1 kg/15 mm = 3.73 lb/in.
- Zero-span breaking length = kg breaking load \times 200,000/[basis weight/sq in \times 3].
- Sample size is (1 \times 5) cm.

RESULTS AND DISCUSSION

Membrane's preparation

Grafting process

Different parameters affecting and controlling the grafting process namely, monomer and initiator concentration, polymerization time and temperature, and finally solvent composition were studied, and the obtained results are discussed in the following. The mechanism of grafting process is illustrated in Scheme 1.

Effect of monomer concentration

Diffusibility of monomers into the polymer matrix has a great influence on the grafting process. The effect of monomer concentration on the GP%, GE%,

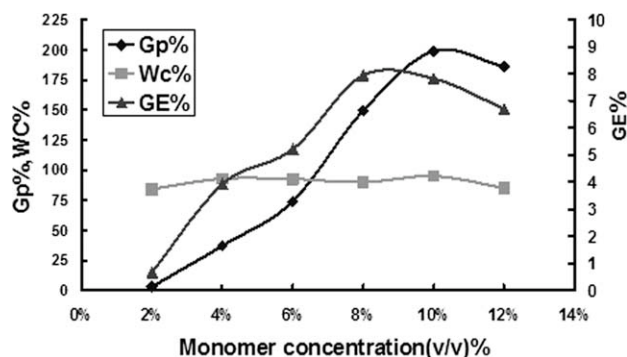


Figure 2 Effect of monomer concentration on the percentage of grafting, grafting efficiency, and weight conversion.

and total WC% was investigated. Figure 2 shows that increasing the monomer concentration clearly increased the percentage of grafting and GE%. Maximum GP was obtained at 10% GMA solution and then almost tends to level off, whereas the GE% reaches maximum at 8% GMA and then tends to decrease slightly with further increase of GMA. These observations may be attributed to the following explanations:

1. Increasing the monomer concentration up to 10% facilitates the diffusibility of monomer toward the initiated sites on the cellulosic chains of cellophane membranes, which consequently increase the grafting yield.
2. At monomer concentrations higher than 10%, the rate of radical formation from the monomer becomes greater when compared with that of rate of diffusion through the polymer matrix, and a homopolymer is formed as a layer on the membrane's surface reducing, as a sequence, the diffusivity of GMA monomer; and hence, the GP and efficiency tend to decrease.

Effect of initiator concentration

Figure 3 shows the effect of KPS concentration variation on the studied grafting parameters. It is clear that increasing the initiator concentration from 0.004 to 0.01M is accompanied by significant increase in the grafting percentage. Further increase of the concentration beyond 0.01M results in the leveling off of GP%. On the other hand, the WC% remains practically constant with increasing the initiator concentration beyond 0.006M. This may be due to the fact that partial blockage of the internal membranes structure has been occurred by the hydrophobic PGMA graft side chains.

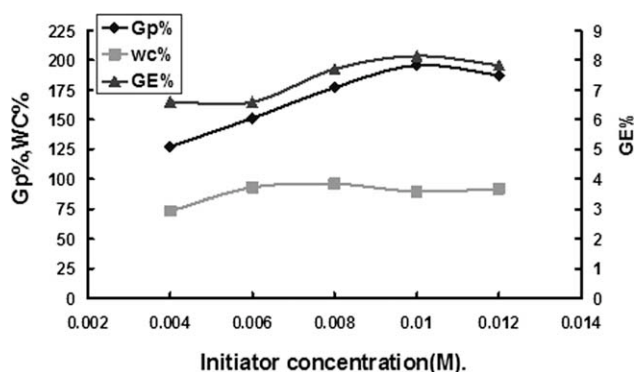


Figure 3 Effect of initiator concentration on the percentage of grafting, grafting efficiency, and weight conversion.

Effect of grafting temperature

Effect of the polymerization temperature variation on the grafting parameters is illustrated in Figure 4. A substantial increase in the GP% and GE% is observed with increasing the temperature from 35 to 55°C. This enhancement in grafting of GMA onto cellophane membranes on raising the polymerization temperature might be attributed to the following favorable effects of temperature on:

1. Diffusion of GMA from the solution phase to the swellable cellulose phase.
2. Increasing the solubility of the monomer.
3. Increasing the rate of thermal dissociation of KPS and hence the GMA rate of free radical formation on the membrane backbone.
4. Formation and propagation of grafted chains

The net effect of all such factors leads to high grafting yield with increasing the polymerization temperature. Further increase of the polymerization temperature beyond 55°C resulted in decrease of both GP% and GE%. This could be attributed to the formation of homopolymer film of hydrophobic nature on the surface of cellophane membranes. Because PGMA did not dissolve in the monomer solution, it creates a diffusion barrier preventing the

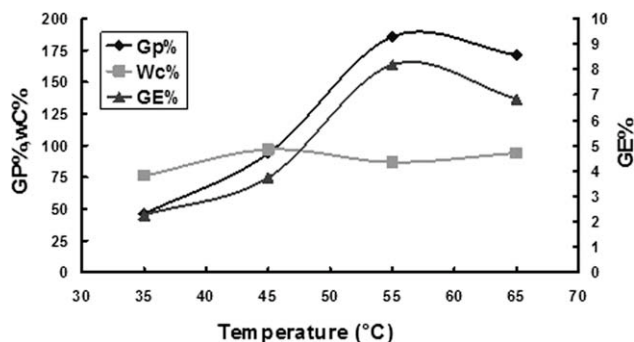


Figure 4 Effect of temperature on the percentage of grafting, grafting efficiency, and weight conversion.

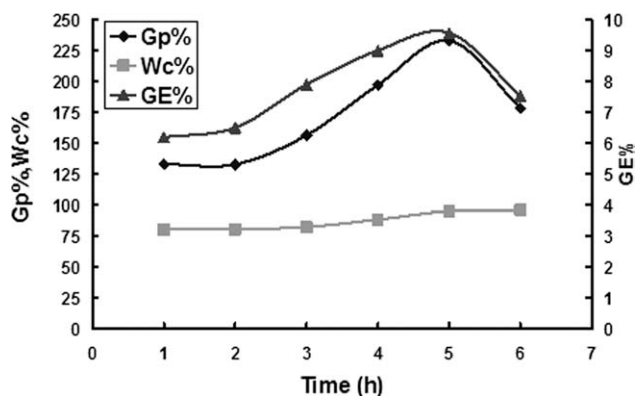


Figure 5 Effect of time on the percentage of grafting, grafting efficiency, and weight conversion.

monomer from reaching to the cellulosic backbone, which leads to the formation of homopolymer on favorite of grafting process.

Effect of grafting time

The effect of grafting time variation on the grafting parameters is illustrated in Figure 5. The results reveal that increasing the grafting time from 1 to 5 h increases the GP% and GE% in the same manner to reach maximum values at 5 h of grafting time. This kind of behavior may be referred to the combination of two processes. The first increases the number of formed free radicals on both monomer solution phase and polymer solid phase. Simultaneously, in parallel with that, the amount of diffused monomer into the polymer phase increased during postgrafting time. The combination of the two processes leads finally to increase both GP% and GE%. On the other hand, further increase of the reaction time to 6 h affected negatively both GP% and GE%. This could be explained by the favorite of homopolymer formation over the grafting process. Because the homopolymer is hydrophobic, its precipitation on the surface of membrane creating diffusion barrier reduced the amount of diffused monomer into the polymer matrix and hence the GP% and GE%.

Effect of solvent composition

Figure 6 shows the effect of variation solvent composition on the parameters of the grafting process. It can be observed that the GP% and GE% increased linearly with increase in ethanol percentage to reach maximum values at 50% ethanol aqueous solution then tends to level off. This could be explained by increasing the solubility of GMA, which, in turn, facilitates its diffusion into the polymer matrix. On the other hand, ethanol acts as a reducing agent,

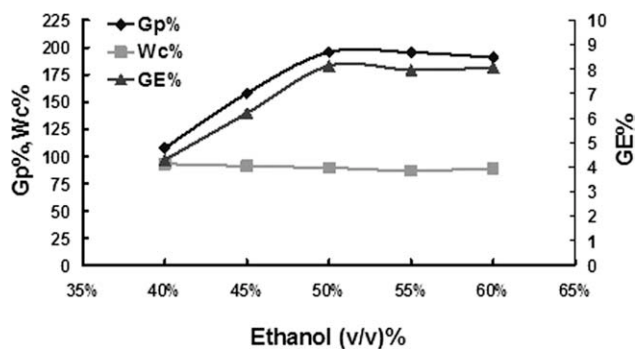


Figure 6 Effect of solvent composition on the percentage of grafting, grafting efficiency, and weight conversion.

which facilitates the process of KPS oxidation to form free radicals.

Amination process

Different parameters affecting and controlling the amination process namely; EDA concentration, amination time, and temperature were studied, and their effect on the IEC of the prepared membranes was monitored. The obtained results are discussed in the following. Furthermore, the mechanism of amination process is illustrated in Scheme 2.

Effect of EDA concentration

The effect of variation ethylene diamine (EDA) concentration on the IEC of cellophane-modified membranes is illustrated in Figure 7. From the figure, it can be seen that there is a linear increase of IEC with increase in EDA concentration from 1 to 5%. Further increase of EDA concentration to 6% has no significant effect. This behavior may be referred to increase formation of imides groups, which subsequently subjected to doping by phosphoric acid.

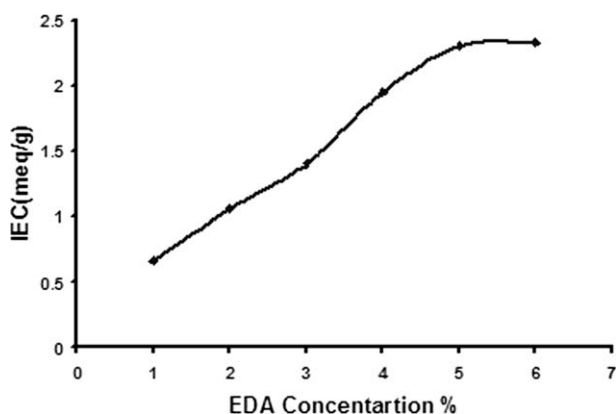


Figure 7 Effect of EDA concentration variation on the ion exchange capacity.

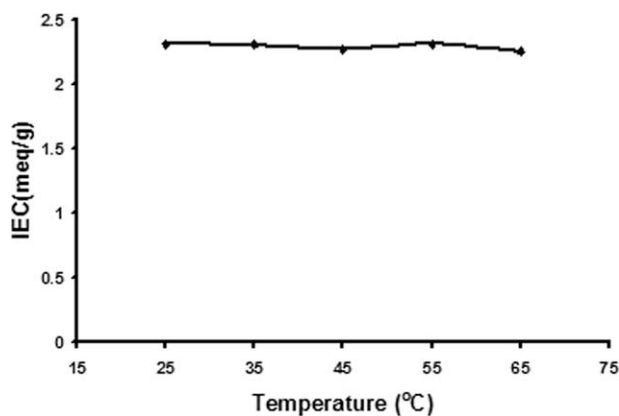


Figure 8 Effect of temperature variation on the ion exchange capacity.

Effect of reaction temperature

The effect of variation reaction temperature with EDA on the IEC of cellophane-modified membranes is shown in Figure 8. The figure shows that the IEC almost does not affect with increasing temperature from 25 to 65°C. Elevating reaction temperature normally leads to increasing the reaction rate through facilitating the diffusion of EDA into the polymer backbone interior, which consequently leads to improve the membranes hydrophilicity. Long reaction time, 8 h, in addition to thinner membrane helps in the same direction of accelerating the reaction and hence reduced the effect of elevation the reaction temperature.

Effect of reaction time

The effect of variation reaction time with EDA on the IEC of cellophane-modified membranes is shown in Figure 9. It can be noticed that the IEC increases with the increasing time of reaction. Two stages have been observed. The first stage ranged from 2 to

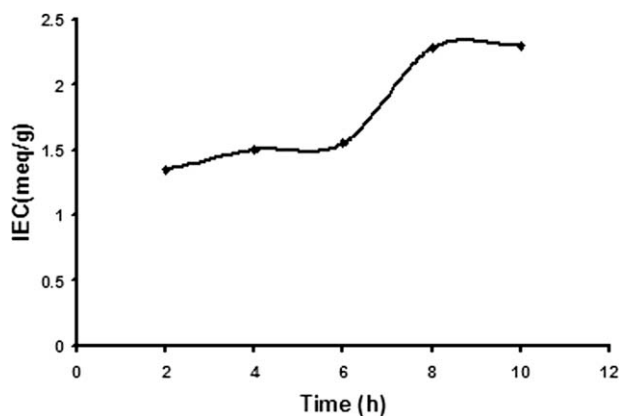


Figure 9 Effect of variation time on the ion exchange capacity.

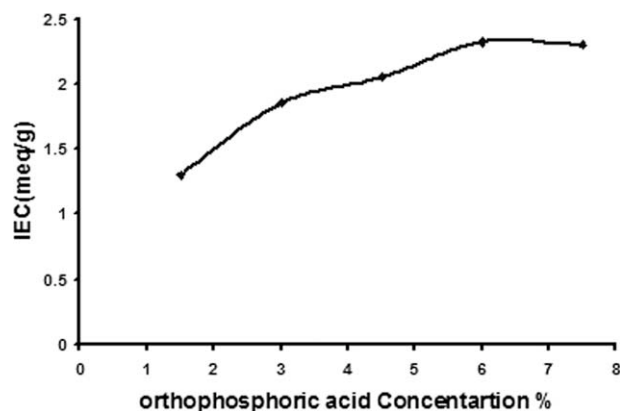


Figure 10 Effect of orthophosphoric acid concentration variation on the ion exchange capacity.

6 h. The IEC of modified cellophane membranes was increased slightly. The second stage, up to 8 h, the IEC increased significantly to reach maximum value and then leveled off with further increase of reaction time to 10 h. This behavior could be interpreted based on the occurring of reaction between imides group on the surface of membranes and phosphoric acid, which leads to the formation of clouds of phosphoric acid on the membrane surface. These clouds retarding the diffusion of further phosphoric acid molecules to the amine groups located in the pores of the membranes. Within 8-h reaction time, the excess of OPA molecules diffused into pores and as results the IEC increased.

Phosphorization (doping) process

Effect of OPA concentration

The effect of variation orthophosphoric acid (OPA) concentration on the IEC of cellophane-modified membranes is shown in Figure 10. Inspection the figure indicates that there is an increase of IEC with increasing of OPA concentration. Maximum IEC was obtained at 6% OPA and then tends to level off. This behavior may be attributed to the increase of OPA concentration gradient between the liquid phase and the polymer phase (membrane). This gradient will lead to the increase in the diffusion of OPA into the bulk of the membranes structure through its pores and, as a result, increase the number of attached OPA which expressed as IEC increase.

Effect of reaction temperature

The effect of variation reaction temperature on the IEC of cellophane-modified membranes is shown in Figure 11. From the figure, it can be observed that the IEC does not affect with the elevation temperature from 25 to 65°C. This trend could be explained according to the hydrophilic nature and small thick-

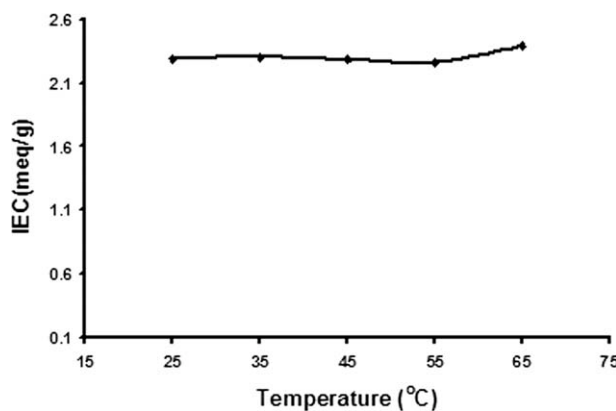


Figure 11 Effect of temperature variation on the ion exchange capacity.

ness of the membranes in addition to long reaction time. The sum of all above-mentioned factors eliminate the effect of reaction temperature on the reaction rate and consequently on the IEC.

Effect of reaction time

The effect of variation reaction time on the IEC of cellophane-modified membranes is illustrated in Figure 12. This figure shows that the IEC increases with increase in reaction time to reach maximum values after 8 h and then levels off. This is an expected behavior due to the pores nature of the membranes, which needs time to diffuse phosphoric acid molecules to attach the imides groups inside the pores.

Membrane's characterization

Water and methanol up-take

Water absorption in cellulose films is attributed mostly to the hydroxyl groups located on polysaccharides units. Nearly, one-third of the cellulose in cellophane membranes are amorphous in nature and

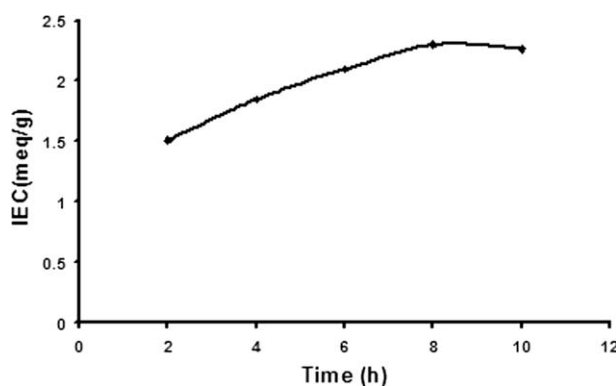


Figure 12 Effect of time variation on the ion exchange capacity.

TABLE I
Water Uptake for Ungrafted, Grafted, Aminated, and Phosphorized Membranes

Gp (%)	Water uptake of grafted membranes (%)	Water uptake of amination membranes (%)	Water uptake of phosphorized membrane (%)
0	65.44	–	–
2.93	55.00	66.32	41.04
37.20	44.00	92.00	58.80
74.00	36.00	48.40	21.05
149.38	15.00	17.35	11.01
185.78	9.00	10.28	5.59
198	5.00	6.78	1.86

are responsible for water absorption, while crystalline zones being impenetrable. The water and methanol uptake of various grafted cellophane membranes together with that of ungrafted, aminated, and phosphorized cellophane membranes are presented in Tables I and II. The data clearly indicate that the water uptake of the grafted cellophane membranes progressively decreased as the extent of grafting increased. This may be due to the fact that partial blockage of the internal membranes structure has been occurred by the hydrophobic PGMA graft side chains. These results are in agreement with the results obtained by the authors.³⁰ It is clear from Table I that the water up take percent for all aminated membranes is more than that of grafted cellophane membrane under the same grafted percentage. The case was different for phosphorized membranes in which its water uptake was found less than that of its native counter part. On the other hand, the methanol uptake behavior is almost the same except the phosphorized membranes have higher methanol uptake than the native cellophane membrane.

Dimensions changes

Tables III and IV show the dimension changes as a result of water and methanol uptake of various

TABLE II
Methanol Uptake for Ungrafted, Grafted, Aminated, and Phosphorized Membranes

Gp (%)	Methanol uptake of grafted membranes (%)	Methanol uptake of amination membranes (%)	Methanol uptake of phosphorized membrane (%)
0	22.08	–	–
2.93	22.27	23.69	41.34
37.20	14.51	13.88	23.68
74.00	13.738	16.346	21.088
149.38	15.180	13.764	10.87
185.78	4.616	4.753	11.19
198	3.043	1.07	2.99

TABLE III
Dimensions Changes in Water Uptake for Ungrafted, Grafted, Aminated, and Phosphorized Membranes

Gp (%)	Dimensions changes of grafted membrane (%)	Dimensions changes of amination membrane (%)	Dimensions changes of phosphorized membrane (%)
0	11.50	–	–
2.93	11.05	13.61	11.57
37.20	12.38	12.45	14.70
74.00	6.92	10.09	7.46
149.38	6.71	6.35	7.50
185.78	2.75	4.16	1.31
198	2.600	3.00	1.70

grafted cellophane membranes in comparison with ungrafted, aminated, and phosphorized cellophane membranes. The data indicate that the dimension changes resulted upon water up take for all modified membranes are almost the same under the same grafted percentage. The same behavior was observed upon methanol uptake.

Mechanical characterization

TS and elongation (E) at break were measured on rectangular strips. TS indicate maximum stress developed in a film during a TS test while E indicates capacity of the film to stretch.³¹ The tensile properties of ungrafted and different percentage grafted membranes were measured and recorded in Table V. 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 increase as a result of phosphorization. This means that after phosphorization, modified membranes became more elastic than the ungrafted one. In general, improvement of the mechanical properties of cellophane-modified membranes has been obtained.

TABLE IV
Dimensions Changes in Methanol Uptake for Ungrafted, Grafted, Aminated, and Phosphorized Membranes

Gp (%)	Dimensions changes of grafted membrane (%)	Dimensions changes of amination membrane (%)	Dimensions changes of phosphorized membrane (%)
0	12.344	–	–
2.93	10.185	2.683	11.574
37.20	4.125	4.125	6.720
74.00	1.705	1.681	8.082
149.38	1.611	1.611	5.035
185.78	1.344	1.102	1.312
198	0.368	1.94	0.62

TABLE V
Tensile Strength and Elongation Occurred on Ungrafted Cellophane Membrane and Phosphorized Cellophane Membrane

Gp (%)	Tensile strength (N)	Elongation (mm)
0	11.00	1.83
2.93	12.65	2.09
37.20	15.50	2.251
74.00	18.00	2.7
149.38	18.34	2.94
185.78	25.15	3.54
198	23.06	2.623

Membrane thickness changes

Because of the grafting of the PGMA onto the cellophane membranes, the thickness of the membranes has been changed. Figure 13 shows the changes in membranes thickness as measured by micrometer against the grafting percent. It is clear from the graph that the thickness of the grafted membranes increases with increase in the grafting percentage. This may be explained as a result of the incorporation of the PGMA chains onto the matrix of cellophane membranes.

Infrared spectrophotometric analysis

Figure 14 illustrates the FTIR spectra for ungrafted, grafted, aminated, and phosphorized cellophane membranes. The appearance of characteristic absorption band for $\text{C}=\text{O}$ at 1724 cm^{-1} and three characteristic bands for epoxy rings at $1238\text{--}1255$, 840 , and 750 cm^{-1} (Curve b) provided evidence of occurring grafting process of PGMA. Opening of the epoxy rings through amination process has been proved through the appearance of characteristic bands for NH_2 group at 3357 cm^{-1} . The remaining characteristic band for epoxy rings indicates in complete aminated reaction (curve c). With phosphoric acid doping, a very broad absorption band complex appears in the wave number range from about $2500\text{--}3000\text{ cm}^{-1}$.³²

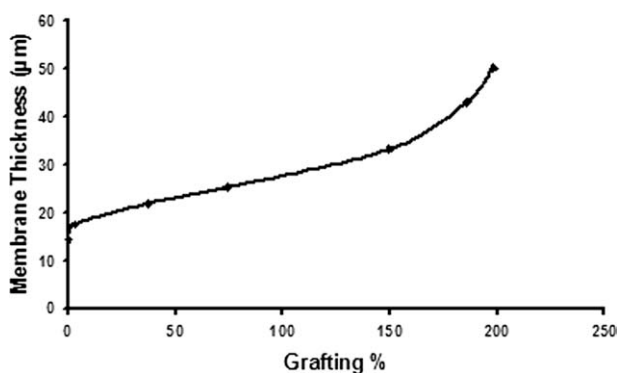


Figure 13 Effect of grafting percentage on the thickness of grafted membranes.

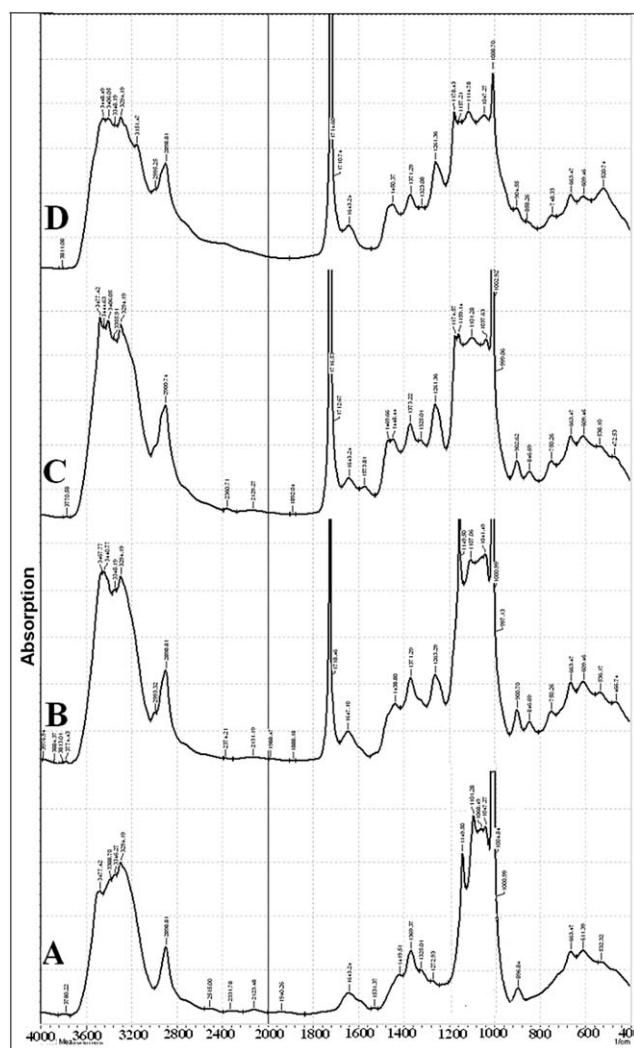


Figure 14 FTIR spectra of (A) ungrafted, (B) 74% grafted, (C) aminated, and (D) phosphorized membranes.

Thermal gravimetric analysis

Thermal gravimetric analysis for modified and unmodified cellophane membranes was carried out by TGA analyzer under nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$.²⁵ It is clear from Figure 15 that weight loss in case of ungrafted membranes occurs after 280°C at a relatively high rate up to 350°C , where the membrane lost about 50% of its original weight. Above this temperature, the rate of weight loss becomes lower. On the other hand, grafted membranes show different behavior probably because of the gained thermal stability of the membrane when compared with the ungrafted membrane (curve B). The weight loss at 350°C has been reduced to reach 22% when compared with 68% in the case of ungrafted membranes. This behavior could be attributed to the formation of graft copolymer between PGMA and the cellulose backbone. T_{50} , the temperature needed to loss 50% of the membrane original weight, has been show in

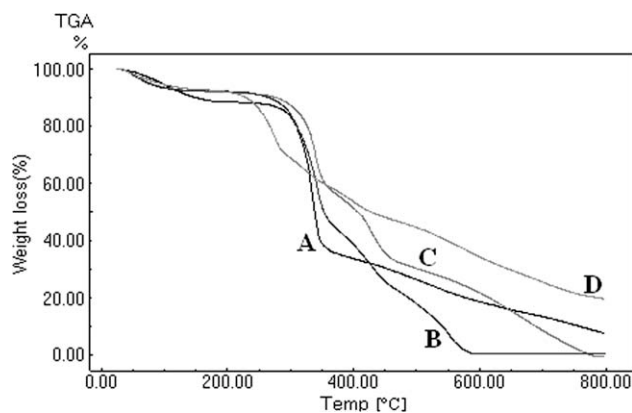


Figure 15 TGA thermographs of (A) ungrafted, (B) 74.00% grafted, (C) aminated, and (D) phosphorized membranes.

Table VI. It is clear that shift to higher temperature, 370°C with grafted membranes, 420°C with aminated membranes, and, 450°C with phosphorized membranes compares to 350°C of ungrafted ones.

It is clear from data tabulated earlier that T_{50} for all modified membranes is more than that of original cellophane membrane, which indicates that the modified membranes are more thermally stable than original cellophane membrane. Comparing these results with that obtained from Nafion modification, it is clear that the strategy for modification has been successful in inducing remarkable thermal stability, which is known as a fundamental requirement for poly electrolyte exchange membranes in DMFC. The obtained results are in agreement with published results by Reddy et al.³³ where treated cotton fabrics lost 53% at 500°C compared to 84% of untreated fabrics. They referred the obtained results to increase char formation of fire-retardant cotton fabrics in the presence of phosphorous compounds.

Scanning electron microscope analysis

Figure 16 displays SEM pictures for the ungrafted cellophane, cellophane-g-GMA, aminated, and phosphorized membranes. It is clear from the figures that no phase separation has been observed upon different modification steps. It is clear that the changes in structure as a result of the modification grafting process and subsequent aminated and phosphorized process have been proved. No compactness or cracks were observed.

Ion exchange capacity

Ion exchange capacity (IEC) indicates the density of ionizable hydrophilic groups in the membrane matrix, which are responsible for the IC of the membranes, and this is an indirect approximation of the proton conductivity³⁴, which is one of the main

objectives of application the proton exchange membranes in DMFCs application.

As seen, the IEC of the modified membranes is greatly improved compared to ungrafted cellophane membrane, and the IEC is exponentially decreased with the increase in the grafting extent. Figure 17 shows that maximum IEC was obtained at 37.20% grafting percentage and then tends to decrease followed by leveling off at grafting percentage starting from 185%. This behavior may be attributed to reduce the chance of formation imides groups through consumption of diamine in crosslinking process between two epoxy rings of PGMA grafted chains. As a result, the number of imides groups available to attach OPA have been reduced and as a sequence the IEC. This explanation is supported by the water uptake results. It is generally accepted that a water uptake is directly related to the concentration of ionic sites, that is, PO_4^- groups. Seo et al.²⁴ reported that water uptake is not consistent with the IEC behavior of the membranes. It is presumably due to the fact that more crosslinking of membranes lead to more rigid and compact structure of the membranes. Compared to Nafion 117 membranes, the minimum IEC obtained with grafting percentage from 185 to 200% is almost equal. The maximum IEC obtained value, 2.2 meq/g, is almost 2.5 times of Nafion was obtained with 37% grafting percentage membranes.

Methanol permeability measurements

In this work, the methanol permeability for the grafted membrane, in comparison with that of ungrafted membrane, was determined using a diffusion cell in which the membrane was clamped between two reservoirs of 2M methanol and distilled water. Because the low methanol permeable with higher IC membranes is the important requirement for proton exchange membranes in DMFCs, we focused on the measurements of the methanol permeability for the modified membranes. The concentration of methanol in water reservoir was followed

TABLE VI
The Temperature Needed to Loss 50 % of The Membrane Original Weight

Gp (%)	T_{50} of grafted membranes	T_{50} of amination membranes	T_{50} of phosphorized membranes
0	345	–	–
2.93	345	355	360
37.20	350	360	405
74.00	360	405	430
149.38	360	410	430
185.78	370	420	450
198	370	420	450

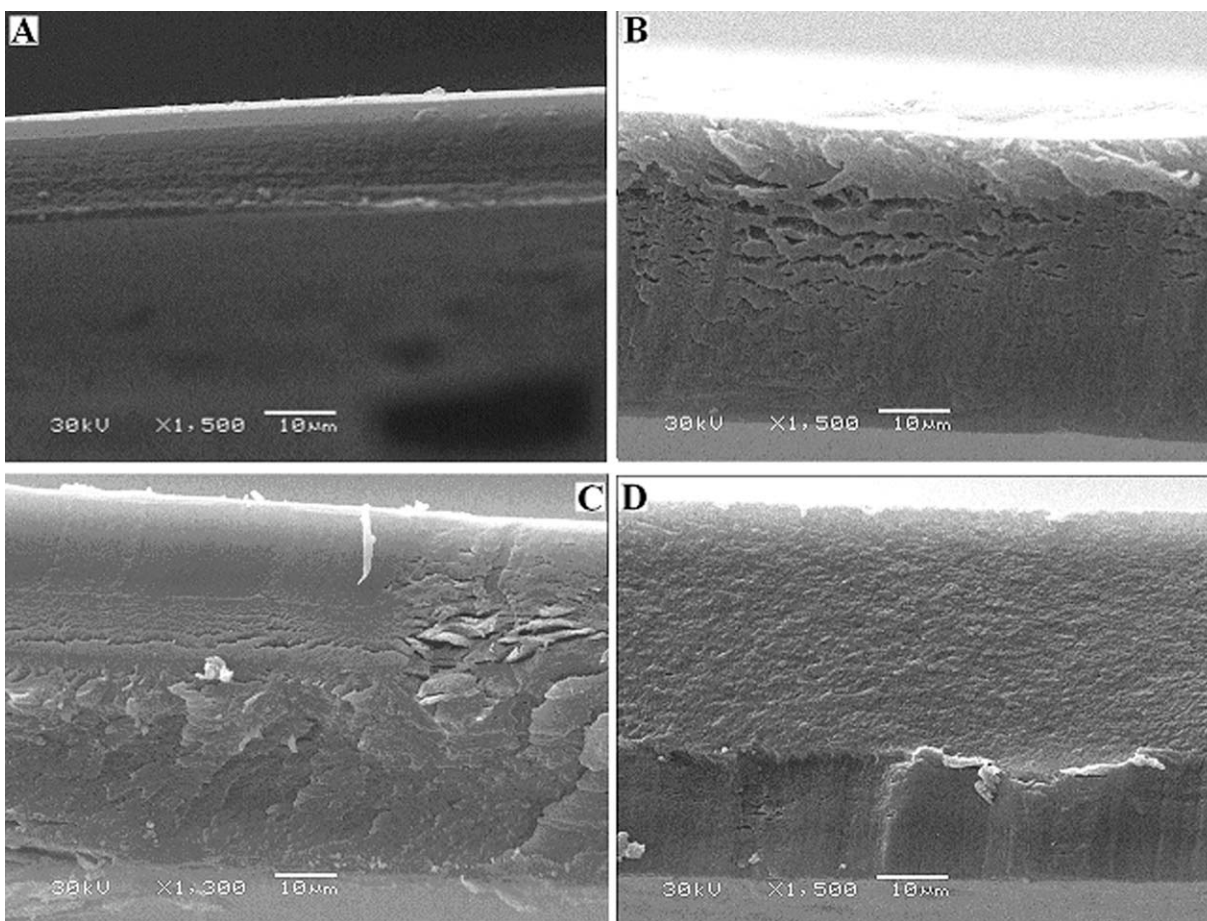


Figure 16 SEM micrograph (1500) of (A) original cellophane, (B) grafted [198%], (C) aminated, and (D) phosphorized membranes.

using gas chromatographic analysis to estimate the methanol permeability for all membranes under the investigation. In general, the methanol concentration in the water compartment for all the modified membranes is lower than that for the native one. From Figure 18, it is concluded that the methanol permeability of modified membranes is lower than that of

cellophane membrane, and it is decreased with increasing the grafted polymer content in the original cellophane membrane. The reduction in methanol permeability may be due to the incorporation of PGMA chains into the cellulose matrix, which leads to the decrease in the modified membranes pores volume than that of virgin cellophane and therefore

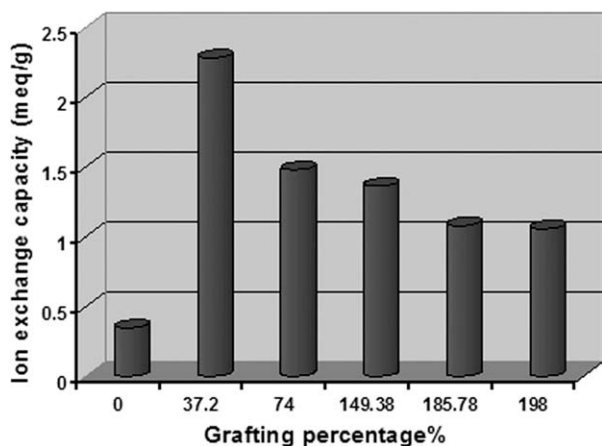


Figure 17 IEC for ungrafted and grafting percentage of cellophane membrane.

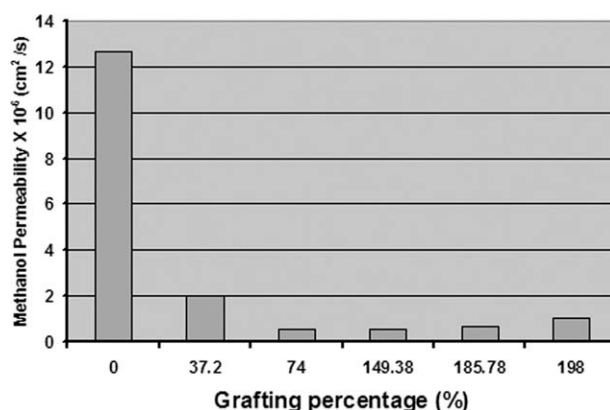


Figure 18 Effect of grafting percentage on the methanol permeability of the modified membranes in comparison with ungrafted cellophane membrane.

lowering the methanol permeability. This explanation is supported by the methanol uptake data. It is worthy to mention here that the methanol permeability for Nafion 117 membrane under the same conditions is 3.4×10^{-6} ($\text{cm}^2 \text{ s}$). This value is almost 70% higher than the maximum value and 8.5 folds of the minimum value of the prepared modified cellophane membranes. Nafion nanocomposite membrane modified by phosphoric acid shows a reduction of the methanol permeability.³⁵ Minimum value of 1.0×10^{-7} ($\text{cm}^2 \text{ s}$) was obtained using 5 wt % MeOH compared to 4.7×10^{-7} ($\text{cm}^2 \text{ s}$) of our modified membranes. Nevertheless, our membrane was tested using 15 wt % MeOH. Pu et al.³⁶ prepared a new anhydrous proton conducting material based on phosphoric acid-doped polyimide with very low methanol permeability in the range of $2\text{--}7.5 \times 10^{-8}$ ($\text{cm}^2 \text{ s}$). However, they tested methanol permeability under lower methanol concentration and temperature compared to our membranes.

Ionic conductivity

The membrane samples were characterized by EIS to determinate their proton conductivity. The results are reported in Table VII.

The membranes samples 1–3 and Cellophane blank were damaged during the EIS experiments, and it was not possible to determinate their proton conductivity. A possibility to increase their stability is to produce more thick samples.

Despite the Nafion membrane resulted to be more conductive than the our prepared samples, still interesting to note is that the proton conductivity increased from sample 4 to sample 6 with grafting percentage (Fig. 19). Possible crosslinking process through bridging two epoxy rings with one molecule of EDA, which consequently leads to reduce of the available terminal amine groups for further doping with phosphoric acid, is a reasonable explanation for

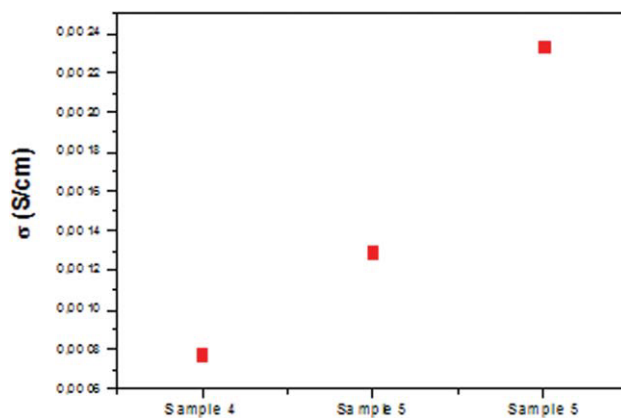


Figure 19 Ionic conductivity for Nafion, modified cellophane membranes with different grafting percentage and ungrafted cellophane membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the obtained low IC. Compromise between the thermal, mechanical characters of the prepared membranes, and its IC is the real challenge in the running experiments now in our laboratories addressing this topic. Other future direction is using homogeneous grafting process with cellulose followed by casting process for the membranes. This technique will allow us to have membranes with variant thickness. Direct reaction between epoxy rings in the PGMA-grafted chains and phosphoric acid is also currently tried.

CONCLUSIONS

Modified cellophane membranes for DMFCs have been prepared, characterized. In the part of membrane preparation, the functionalization process through grafting of cellophane membranes with PGMA using persulphate initiation system has been studied by exploring the effect of different factors, such as monomer, initiator concentration, time, temperature, and solvent ratio. Different GPs have been obtained and controlled as a result of the variation of the grafting conditions. The occurrence of grafting has been proved by FTIR, TGA, and SEM. The introduced epoxy groups of PGMA are subsequently converted into amine groups by amination process using EDA then doped with phosphoric acid ($-\text{PO}_3\text{H}$) groups, which significantly contributed to enhancing IEC and IC. The mechanical properties and the thermal stability of modified membranes increased with their thickness, which increases with the grafting percentage. The methanol permeability of modified membranes is lower than that of cellophane membrane, and it is decreased with increasing the grafted polymer content. The IC of the prepared modified cellophane membranes was found

TABLE VII

Ionic Conductivity of Cellophane, Modified Cellophane, and Nafion Membranes

Sample	d (μm)	R (Ω)	σ (S cm^{-1})
Sample 1	14	^a	^a
Sample 2	20	^a	^a
Sample 3	20	^a	^a
Sample 4	41 ^b	8.39	0.000768
Sample 5	18	2.19	0.00129
Sample 6	21	1.42	0.00233
Cellophane blank	12	^a	^a
Nafion blank	177	0.718	0.0388

^a The sample was broken during the test.

^b The membrane was folded and it was impossible to open it without damaging. The sample characterized was formed by two layers of membrane.

less than that of Nafion ones. Despite that, the IC increases with the grafting percentage. The main advantage of our prepared membranes is the incomparable low costs with Nafion. Further modification and optimization of the experimental conditions and techniques are required to improve the IC of our membranes with taking into consideration not losing of the acquired thermal, mechanical, and low-methanol permeability characters.

References

1. Heinzel, A.; Barragan, V. M. *J Power Sour* 1999, 84, 70.
2. Beatie, P. D.; Orfino, F. P.; Basura, V. I.; Zychowska, K.; Ding, J.; Chuy, C.; Scmeisser, J.; Holdcroft, S. *J Electroanal Chem* 2001, 503, 45.
3. Lasségues, J. C. In *Proton Conductors, Solids, Membranes and Gels—Materials and Devices*; Colomban, Ph., Ed.; Cambridge University Press: New York, 1992; p311–328.
4. Jones, D. J.; Rozière, J. *J Membr Sci* 2001, 185, 41.
5. Wainright, J. S.; Litt, M. H.; Savinell, R. F. In *Handbook of Fuel Cells, Vol.3*; Vielstich, W., Lamm, A., Gasteiger, H. A., Eds.; Wiley: New York, 2003; p436.
6. Kerres, J. A. *J Membr Sci* 2001, 185, 3.
7. Gillespie, R. J.; Robinson, E. A. In *Nonaqueous Solvent Systems*; Waddington, T. C., Ed.; Academic Press: New York, 1965; pp117–210.
8. Dabrowska, A.; Stys, S.; Wieczorek, W.; Przulski, J. *Proceedings of the first international symposium on new materials for fuel cell systems*, Montreal, Canada, 1995; Electrochemical Society, Inc.: Pennington, NJ, 1995; p95.
9. Donoso, P.; Gorecki, W.; Berthier, C.; Defendini, F.; Poinsignon, C.; Armand, M. B. *Solid State Ionics* 1988, 28–30, 969.
10. Petty-Weeks, S.; Zupancic, J. J.; Swedo, J. R. *Solid State Ionics* 1988, 31, 117.
11. Rogriguez, D.; Jegat, T.; Trinquet, O.; Grondin, J.; Lassegues, J. C. *Solid State Ionics* 1993, 61, 195.
12. Stevens, J. R.; Raducha, D. *Solid State Ionics* 1997, 97, 347.
13. Wieczorek, W.; Stevens, J. R. *Polymer* 1996, 38, 2057.
14. Tanaka, R.; Yamamoto, H.; Shono, A.; Kubo, K.; Sakurai, M. *Electrochim Acta* 2000, 45, 1385.
15. Grondin, J.; Rodriguez, D.; Lassegues, J. C. *Solid State Ionics* 1995, 77, 70.
16. Bozkurt, A.; Ise, M.; Kreuer, K. D.; Meyer, W. H.; Wegner, G. *Solid State Ionics* 1999, 125, 225.
17. Senadeera, G. K. R.; Careem, M. A.; Skaarup, S.; West, K. *Solid State Ionics* 1996, 85, 37.
18. Zaidi, S. M. J.; Chen, S. F.; Mikhaikenko, S. D.; Kaliaguine, S. *J New Mater Electrochem Syst* 2000, 3, 27.
19. Lasségues, J. C.; Grondin, J.; Hernandez, M.; Maree, B. *Solid State Ionics* 2001, 145, 37.
20. Peled, E.; Duvdevani, T.; Melman, A. *Electrochem Solid-State Lett* 1998, 1, 210.
21. Raducha, D.; Wieczorek, W.; Florjanczyk, Z.; Stevens, J. R. *J Phys Chem* 1996, 100, 20126.
22. Zukowska, G.; Rogowska, M.; Weczowska, E.; Wieczorek, W. *Solid State Ionics* 1999, 119, 289.
23. Ericson, H.; Svanberg, C.; Brodin, A.; Grillone, A. M.; Panero, S.; Scrosati, B.; Jacobsson, P. *Electrochim Acta* 2000, 45, 1409.
24. Sco, J. A.; Kim, J. C.; Koh, J. K.; Ahn, S. H.; Kim, J. H. *Ionics* 2009, 15, 555.
25. Mohy Eldin, M. S.; Soliman, E. A.; Hassan, E. A.; Abu-Saied, M. A. *J Appl Polym Sci* 2009, 111, 2647.
26. Nasef, M. M.; Zubir, N. A.; Ismail, A. F.; Khayet, M.; Dahlan, M.; Saidi, H.; Rohani, R.; Ngah, S.; Sulaiman, N. A. *J Membr Sci* 2006, 268, 96.
27. Masahiro, R.; Daisuke, I.; Keiichi, K.; Yuko, T.; Iko, I.; Yoshio, K.; Kohei, S. *J Mol Struct* 2005, 739, 153.
28. Nasef, M. M.; Zubir, N. A.; Ismail, A. F.; Dahlan, K. Z. M.; Saidi, H.; Khayet, M. *J Power Sour* 2006, 156, 200.
29. Fontananova, E.; Trotta, F.; Jansen, J. C.; Drioli, E. *J Membr Sci* 2010, 348, 326.
30. El-Awady, N. I.; El-Awady, M. M.; Mohy El-Din, M. S. *Egypt J Text Polym Sci Technol* 1999, 3, 25.
31. Guadalupe, I.; Oliva and Gustavo V.; Barbosa-Cánovas, L. W. *T. Food Sci Technol* 2008, 41, 359.
32. Li, Q.; He, R.; Berg, R. W.; Hans, A.; Hjuler and Niels J Bjerum. *Solid State Ionics* 2004, 168, 177.
33. Reddy, P. R. S.; Agathian, G.; Kumart, A. *Radiat Phys Chem* 2005, 72, 511.
34. Becker, W.; Schmidt-Naake, G. *Chem Eng Technol* 2002, 25, 373.
35. Kang, J.; Ghil, L.; Kim, Y.; Kim, Y.; Rhee, H. *Colloids Surf A: Physicochem Eng Aspects* 2008, 313–314, 207.
36. Pu, H.; Qiao, L.; Liu, Q.; Yang, Z. *Eur Polym J* 2004, 41, 2505.