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Preparation of Phosphorylated Nata-de-Coco for Polymer Electrolyte Membrane Applications

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ABSTRACT: Fuel cells are being developed to overcome the global energy crisis. The objective of this research is to prepare an environmental-friendly and cheap material as the polymer electrolyte membrane. Coconut water was fermented by *Acetobacter xylinum* to produce nata-de-coco and the phosphorylation was carried out by microwave-assisted reaction. The resulting membranes are characterized by ion exchange capacity, contact angle, proton conductivity, swelling index, methanol permeability, mechanical properties measurement and morphological analysis. At the optimum phosphorylation condition using 17.35 mmol of phosphoric acid, membrane showed a proton conductivity of 1.2×10^{-2} S/cm and a methanol permeability of 2.3×10^{-6} cm^2/s. The tensile strength of the produced membranes increases significantly and the arrangement of the cellulosic fibers are kept well-aligned. It is concluded that a green and sustainable natural resources can be used for preparing electrolyte membrane. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 399–405, 2013

KEYWORDS: batteries and fuel cells; biopolymers and renewable polymers; cellulose and other wood products; membranes

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INTRODUCTION

Fuel cells are considered as important future power sources in overcoming the fossil-based energy crisis. Several types of fuel cells are currently under development, each with its advantages, limitations and potential applications. Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising fuel cell types which use solid polymer as electrolyte.[1–4] Fuel cells are simple to be operated, produce high energy efficiencies, show low CO_2 emissions and hence, are environmental-friendly. PEMFCs and Direct Methanol Fuel Cells (DMFCs) use hydrogen and methanol as their fuel, the latter shows less fuel storage problems.[5] Nafion® is a commercial membrane that is often used for PEMFC due to its high proton conductivity, besides having good chemical and mechanical properties.[6,7] Nevertheless, its high price induces many researchers in the world to find an alternative material. The results of these researches have been published by several groups using different polymers.[4,8–15] At present, many works are being done in this field in order to find cheap fluorine-free materials which can reduce the overall costs of the fuel cell systems.

Highly hydrophilic membranes are marked by the presence of hydroxyl groups in the cellulosic compounds.[16] Iguchi *et al.* showed that lignin-free cellulose, called nata-de-coco, which is produced during the fermentation of coconut water *by Acetobacter xylinum* has high mechanical properties.[17] Our previous work showed that bacterial cellulose can be chemically modified to cellulose acetate by acetylation of hydroxyl groups.[18]

Our preliminary study showed that the proton conductivity of nata-de-coco is quite low, and hence, modifications should be done in order to increase its conductivity. Nata-de-coco film is used instead of powder, because we want to make use of its high mechanical strength which is very beneficial for the application of this material as polymer electrolyte membrane (PEM). Our attempt to sulphonate nata-de-coco films failed because the mechanical properties of the film dropped significantly and it became very fragile. So, finding a method to increase the conductivity of nata-de-coco film without destroying its mechanical properties will be a good approach to obtain an environmental-friendly and cheap PEM material. One alternative has been investigated in this work, namely phosphorylation.

Therefore, the objective of this research is to explore the use of nata-de-coco for electrolyte membrane material by microwave-assisted phosphorylation. The effect of phosphoric acid concentrations on the characteristics of the resulting membranes were studied in terms of proton conductivity, contact angle, degree of swelling, membrane morphology and mechanical properties.

EXPERIMENTAL

Materials

Coconut water and sugar were obtained from the local traditional market, while *Acetobacter xylinum* was taken from the local industry. Other chemicals such as ammonium sulfate, acetic acid, sodium hydroxide, oxalic acid, hydrochloric acid, sulfuric acid, phosphoric acid 85%, urea, *N,N*-dimethylformamide (DMF) were obtained from E. Merck and used without further purification.

Preparation of Nata-de-Coco Films

Nata-de-coco was prepared using the same procedure as our previous experiment.[18] Fermentation was done during 6 days at room temperature and the resulted gels were put in the boiling water for 15 min. Then they were soaked in 1% (w/w) aqueous solution of sodium hydroxide for 24 h, followed by 1% (w/w) aqueous solution of acetic acid for another 24 h. Finally, they were washed in water until the pH was neutral. The nata-de-coco gels were finally pressed at room temperature under an applied pressure of 147 bars for 3 min.

Phosphorylation of Nata-de-Coco Membranes

Phosphorylation of nata-de-coco membranes was conducted using similar reactants described by Wan et al.[19] The difference lied in the reaction condition, in which a microwave irradiation was used instead of a classical thermal reaction. Nata-de-coco was used in the form of film and not in powder because its high mechanical strength is needed for the application as electrolyte membrane. So, an amount of 17.35 mmol of phosphoric acid was mixed with 50 g of urea and dissolved in 100 mL of DMF. A piece of 0.132 g nata-de-coco membrane was then put into the freshly prepared mixture and the reaction was conducted in a 490 Watt microwave oven for 150 s at 130°C. The resulting phosphorylated membrane was washed several times with deionized water to remove all the residual reactants. The reaction was repeated using higher concentrations of phosphoric acid, namely 34.69 mmol and 53.04 mmol, while other conditions were kept constant.

Characterization of Phosphorylated Nata-de-Coco Membranes

Functional groups of nata-de-coco and the phosphorylated one were analyzed by ATR-FTIR spectroscopy using Tensor-27 Bruker spectrophotometer. One milligram of membrane powder was mixed with KBr and mechanically pressed to become KBr pellets. The sample was then put into the sample holder and scanned between 1500 and 850 cm^{-1}. The original nata-de-coco and the phosphorylated ones were characterized using various methods. Their Ion Exchange Capacity (IEC), degree of swelling, contact angle, proton conductivity, and phosphor content were measured. The FTIR spectra were also recorded, while the mechanical properties and morphological structure were observed.

Samples for the IEC measurement were prepared using the procedure described by Smitha.[20] The IEC was calculated using the eq. (1) as follows:

$$\mathrm{IEC} = \frac{(V_b - V_s)[\mathrm{Acid}].f_p}{m} \quad (1)$$

where:

V_b = amount of NaOH solution for the neutralization of blanko solution (mL)

V_s = amount of NaOH solution for the neutralization of the solution containing the membrane (mL)

[acid] = concentration of sulfuric acid (M)

f_p = dilution factor

m = mass of sample (g)

For swelling index measurement, samples were weighed at room temperature and then soaked in deionized water.[19] Membranes were then dried using tissue paper and weighed again. The procedure was repeated until it reached a constant weight. Swelling index (*SI*) was calculated using eq. (2).

$$\%\mathrm{SI} = \frac{m - m_0}{m_0} \times 100\% \quad (2)$$

where

m = mass of wet membrane (g)

m_0 = mass of dry membrane (g)

A contact-angle meter was used for measuring the contact angle of membranes. A sample was put on the plate of this equipment. By using a syringe, 15 μL of water was dropped on the surface of the samples and the lamp was put on to get the projection of droplet contour on a screen. The contact angle of water was then measured.

For the measurement of proton conductivity, a two-probe method was used. The pretreatment of the membrane sample was done by soaking it in 0.1*M* sulfuric acid solution for 24 h in order to protonize all the hydroxyl and phosphate groups. Then the membranes were washed with deionized water repeatedly to remove the residual acids until the pH of the filtrate was neutral. The ionic resistance was measured at 80 °C under a relative humidity of 61.5% using Electrochemical Impedance Spectroscopy (EIS) and platinum as the electrode wire. The frequency range was between 30 Hz and 2 MHz at 10 mV and the measurement was carried out using a LCR meter E4980 A. Proton conductivity was calculated using eq. (3) as follows:

$$\sigma = \frac{l}{RA} \quad (3)$$

where

σ = proton conductivity

l = membrane length

A = membrane surface area

R = ionic resistance

The value of l and A used in this experiment were 1.5 cm and 0.0068 cm^2, respectively.

The permeability of methanol was measured at room temperature by using a diffusion cell containing two different chambers separated by the membrane. The first chamber was filled with a 10% v/v methanol solution in water, while the other one was filled with pure water. The concentration of diffused methanol was determined by gas chromatography technique and the

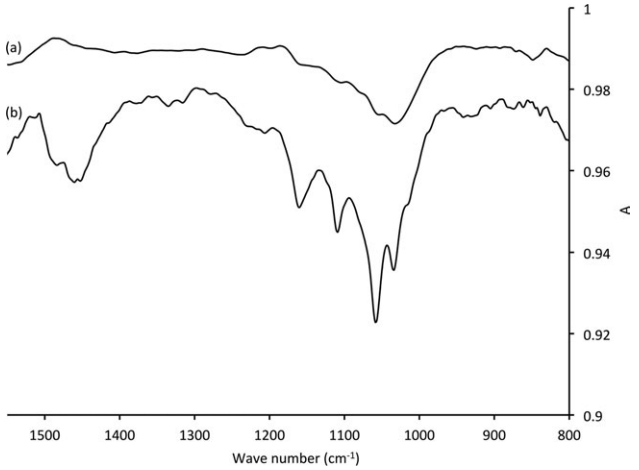

Figure 1. FTIR spectrum of (a) nata-de-coco and (b) phosphorylated nata-de-coco.

permeability of methanol was calculated according to the equation described by Elabd et al.[21] Nafion 117® was used as reference.

For measuring the mechanical properties at room temperature, membranes were cut into standard dumbbell-shaped test samples according to ASTM D638-03. Tensile strength was measured using Autograph tensilemeter, while membrane morphology was measured using SEM Jeol JSM 6360 LA.

RESULTS AND DISCUSSION

Structural Analysis of Original and Phosphorylated Nata-de-Coco Membranes

Figure 1(a,b) show the ATR-FTIR spectra of nata-de-coco and phosphorylated nata-de-coco, respectively. The attribution of some groups vibrating in the zoomed area (1500–850 cm^{-1}) in each compound was described in Table I. New peaks at 1310, 1278, and 1108 cm^{-1} attributed to stretching vibrations of P=O, P—O, and C—O—P groups respectively, appeared after phosphorylation. The presence of C—O—P group proves strongly the formation of cellulose phosphate. This result is in accordance with other research groups who have studied the

Table I. Analysis of ATR-FTIR Spectra of Nata-de-Coco and Phosphorylated Nata-de-Coco

Compound	Wave number (cm^{-1})	Group
Nata-de-coco	1165	C—O—C
	1033	C—O (primary alcohol)
Phosphorylated nata-de-coco	1310	P=O
	1278	P—O
	1165	C—O—C
	1108	C—O—P
	1033	C—O (primary alcohol)

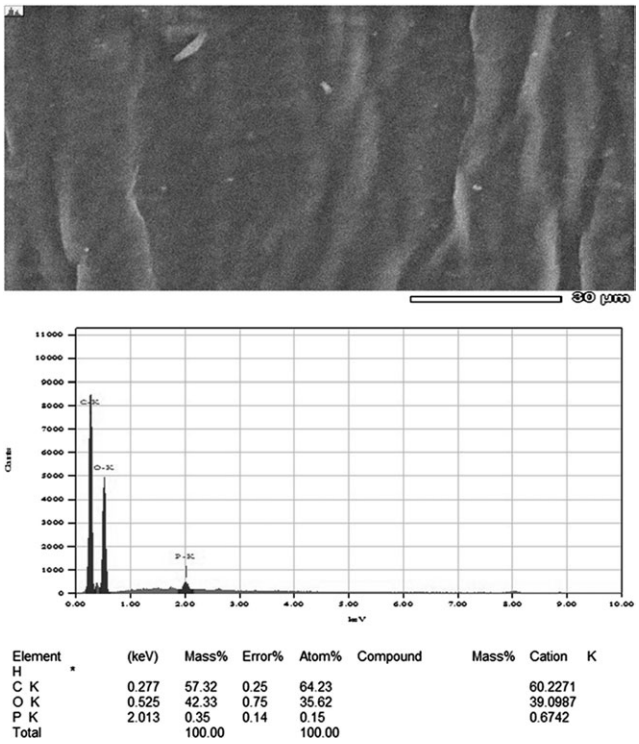

Figure 2. SEM-EDX of phosphorylated nata-de-coco membrane.

mechanism of phosphorylation of cellulose[22,23] and its derivates such as chitosan.[19] Suflet et al. found that the hydroxyl groups at the C-6 position of glucose units were substituted by phosphoric groups which led to the formation of C—O—P linkage. As the reaction proceeds, the intermolecular condensation of phosphates in cellulose polymer chains can form crosslinked polymer.[22]

The SEM-EDX analysis shown in Figure 2 shows that the peaks appeared at 0.277 keV and 0.525 keV are contributed by carbon and oxygen atoms, while phosphor atoms are detected at 2 keV. The mass percentage of C, O, and P are 57.32, 42.33, and 0.67%, respectively. These characterizations prove that the phosphorylation of nata-de-coco has occured in the microwave-assisted reaction forming cellulose phosphate.

Effect of Phosphorylation on Ion Exchange Capacity (IEC) and Proton Conductivity of Phosphorylated Nata-de-Coco Membranes

Figure 3 shows one example of the Cole–Cole plot of phosphorylated nata-de-coco membrane. Ion exchange capacity (IEC) of polymer electrolyte membrane is an important characteristic for fuel cell application since it indicates the amount of ionic groups in the polymer matrix. Figure 4 shows that the addition of phosphoric acid up to 17.35 mmol can increase the IEC and hence, the capacity of proton transfer. This data correlates very well with the corresponding proton conductivity which value is 1.2×10^{-2} S cm^{-1} at 80°C and 61.5% relative humidity. In our experiment the proton conductivity of Nafion 117® obtained at the same condition is 3.9×10^{-2} S/cm. This data shows that the proton conductivity of our environmental-friendly polymer electrolyte membrane reaches the same order as Nafion 117®. It

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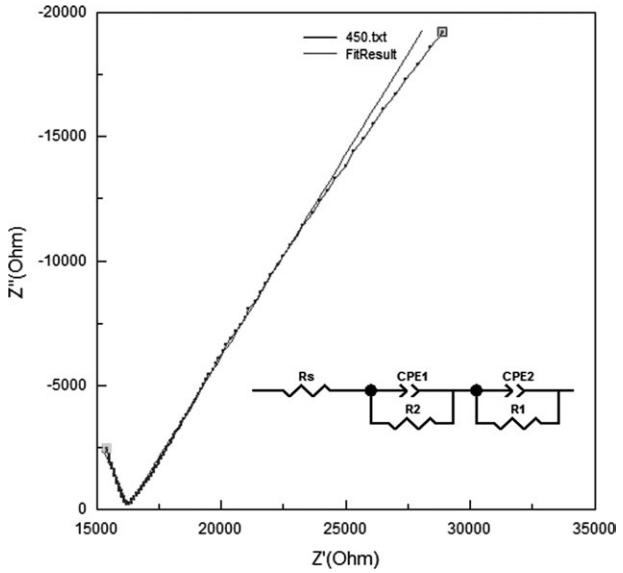

Figure 3. Cole–Cole plot of phosphorylated nata-de-coco membrane.

is known that proton conductivity is affected by various factors such as ion exchange capacity and degree of swelling. So, the amount of charged groups and the sites of mobile ions do affect the proton conductivity.[24] High concentration of phosphoric acid increases the possibility of crosslinks among the polymer chains and hinders the mobility of ions along the polymer network. From this data it can be seen that the optimum condition for the microwave-assisted phosphorylation is 17.35 mmol of phosphoric acid. Although the chemical structure of phosphorylated nata-de-coco is totally different from Nafion®, it has also hydrophilic and hydrophobic domains which enable the proton transport through a cluster-channel network.[25,26] The scheme of proton transport in phosphorylated nata-de-coco is proposed in Figure 5. Since water is present in the media, there is an equilibrium between proton and hydroxyl ions; the latter play the role as counter ions. These counter ions are not drawn in the figure. The formation of cellulose ester makes the proton

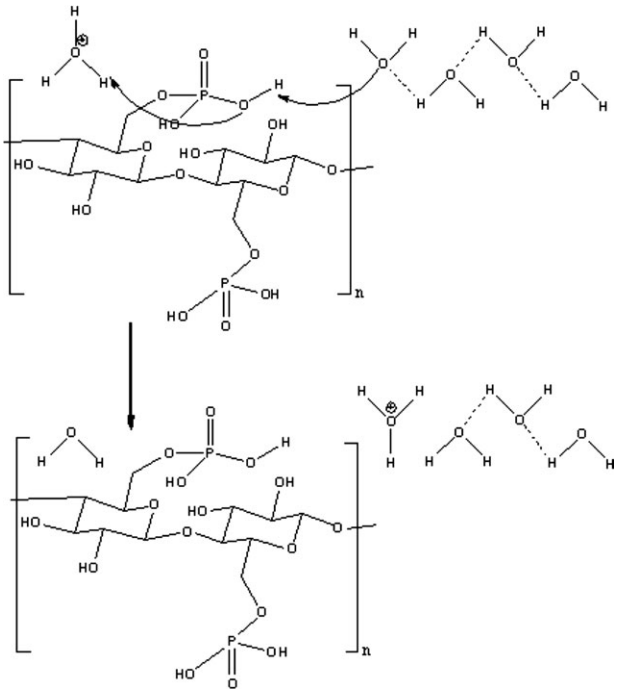

Figure 5. Scheme of proton transport in phosphorylated nata-de-coco membrane.

transfer in the membrane matrix easier, because the $H^{\delta+}$ of the $-O^{\delta-}H^{\delta+}$ in the phosphate group can leave easily and interact with water in its surrounding resulting in protonized water. The $O^{\delta-}$ will also interact with other protonized water, and hence, this kind of interaction creates transfer of protons and increases the proton conductivity of phosphorylated nata-de-coco membrane. Moreover, the formation of hydrophylic channels in the cellulose phosphate is larger than in cellulose, because the phosphate groups are bulkier than hydroxyls. The intermolecular interactions among the polymer chains will decrease and the interactions between the phosphate goups and water will then increase.

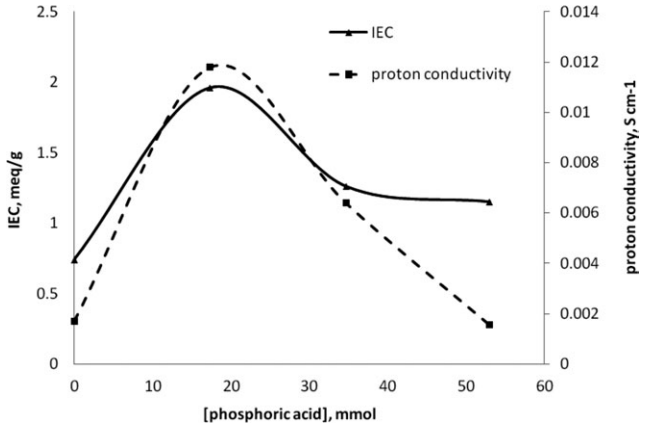

Figure 4. Effect of phosphoric acid concentration on ion exchange capacity (IEC) and proton conductivity of phosphorylated nata-de-coco membranes.

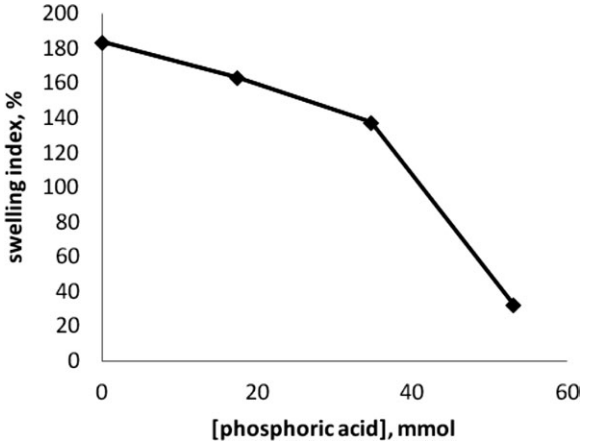

Figure 6. Effect of phosphoric acid concentration on swelling index of phosphorylated nata-de-coco membranes.

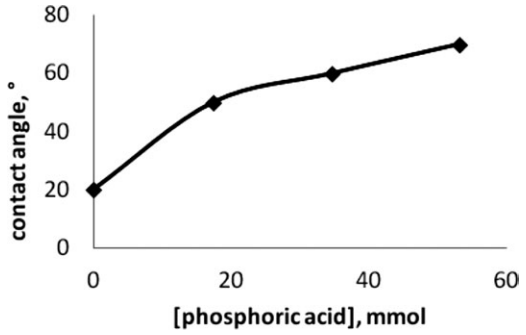

Figure 7. Effect of phosphoric acid concentration on contact angle of phosphorylated nata-de coco membranes.

Table II. Mechanical Properties of Phosphorylated Nata-de-Coco Membranes

Phosphoric acid concentration, mmol	Stress at break (kgf mm^{-2})	Strain at break (%)
0	2.42	1.61
17.35	30.77	0.28
34.69	19.23	0.41
53.04	20.88	0.46

Effects of Phosphorylation on Swelling Index and Contact Angle of Phosphorylated Nata-de-Coco Membranes

As shown in Figure 6, the introduction of phosphate groups into nata-de-coco decreases the swelling index of phosphorylated nata-de-coco. Swelling properties of electrolyte membranes are important since they affect the ion permeability through the membrane. The presence of hydrophilic groups and hydrogen bonding between water molecules and acid are some of the parameters which determine the proton conductivity of polymers.[23,24] The ability of electrolyte membrane to take water determines its ability to transport the protons. Kreuer has pointed out that the presence of water is very important for this process through either Grotthuss mechanism or hydrogen-bond chain mechanism.[27] In the fuel cell applications, membranes should have a moderate degree of swelling in order to get a high ion mobility.[28] Since phosphoric acid also plays as a crosslinker for nata-de-coco and other polymers,[29,30] the crosslinked chains can be formed at high concentration of phosphoric acid. Membranes become less swollen and consequently, their proton conductivity decrease. This corrrelation was also reported by Filho and Gomes.[31] Besides that, the original nata-de-coco has a high hydrophilicity or a low contact angle due to the presence of hydroxyl groups. Figure 7 shows that increasing phosphoric acid concentration resulted in higher contact angle, because phosphorylation has substituted hydroxyl groups with phosphate groups which are less hydrophilic. This data also indicates that the hydrophilicity of the phosphorylated nata-de-

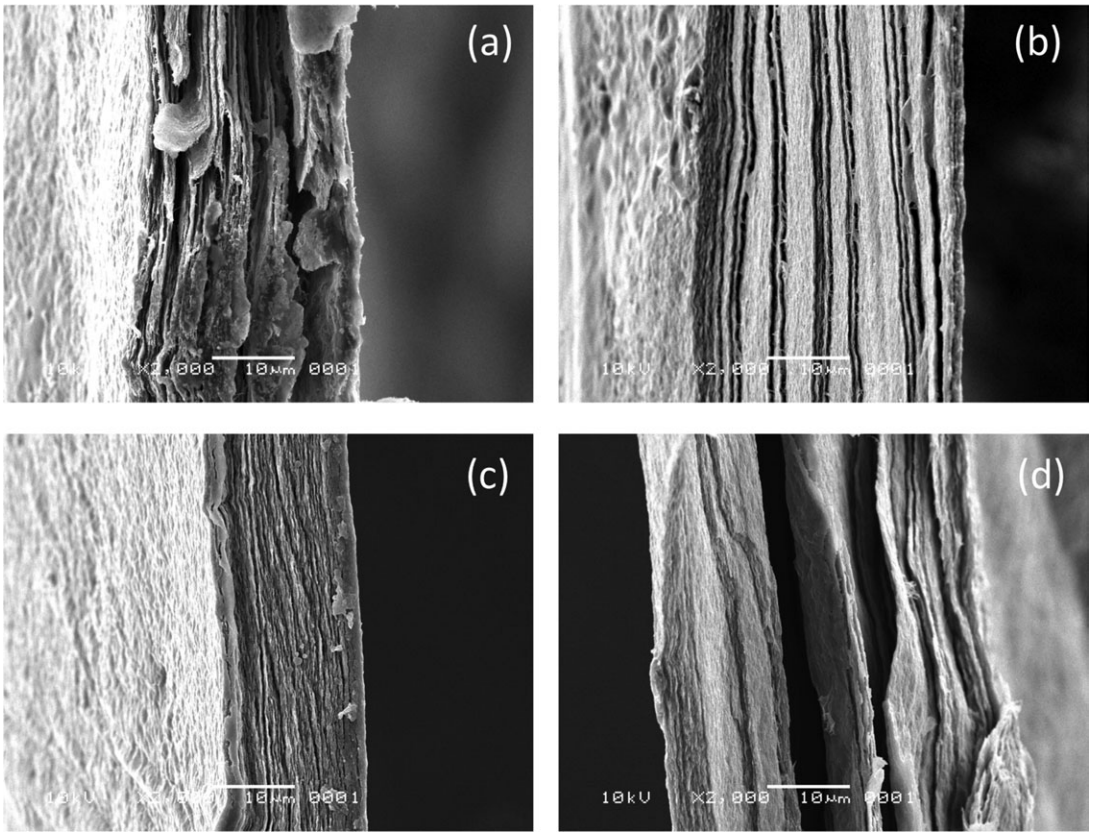

Figure 8. SEM photos: (a) cross-section of nata-de-coco membrane, (b–d): cross-sections of phosphorylated nata-de-coco membrane using phosphoric acid concentration of (b) 17.35 mmol, (c) 34.69 mmol, and (d) 53.04 mmol.

Table III. Proton Conductivity and Methanol Permeability of Phosphorylated Nata-de-Coco and Nafion®

Membrane	Proton conductivity (S/cm)	Methanol permeability (cm^2/s)
Phosphorylated nata-de-coco using 17.35 mmol phosphoric acid	1.18×10^{-2}	2.30×10^{-6}
Phosphorylated nata-de-coco using 34.69 mmol phosphoric acid	6.40×10^{-3}	2.21×10^{-6}
Phosphorylated nata-de-coco using 53.04 mmol phosphoric acid	1.55×10^{-3}	2.13×10^{-6}
Nafion117®	3.90×10^{-2}	5.02×10^{-6}

coco membranes decreases with the concentration of phosphoric acid.

Mechanical Properties and Morphology of Phosphorylated Nata-de-Coco Membranes

Table II shows the mechanical properties of phosphorylated membranes using various concentration of phosphoric acid. Although the data shows some irregularities, a common trend could be observed. Higher acid concentration increased significantly the tensile strength of the produced membranes but decreased their elasticity due to the formation of cross-linked structure. Figure 8 shows the cross-sections of various modified nata-de-coco membranes obtained from different reactions. It can be concluded that the cross-sections of phosphorylated nata-de-coco membranes still keep the regular pattern of well-aligned cellulosic fibers of nata-de-coco, regardless the condition of phosphorylation. This morphology also explains the high mechanical properties of the resulting membranes.

Methanol Permeability of Phosphorylated Nata-de-Coco

Table III shows the proton conductivity and the methanol permeability of the phosphorylated membranes and Nafion 117® as reference. It is found that the proton conductivity varied with the concentration of phosphoric acid, but the methanol permeability was slightly affected. It should be noted that the values of methanol permeability of all the phosphorylated nata-de-coco membranes are about half of its of Nafion 117®. The dense structure of cellulosic layers in the phosphorylated nata-de-coco membranes plays a significant role in decreasing methanol diffusion across the membrane. Based on the experimental data in this work, it can be concluded that the use of 17.35 mmol of phosphoric acid has given the optimum results in terms of ion exchange capacity, proton conductivity and tensile strength.

CONCLUSIONS

In this work we have prepared polymer electrolyte membrane from coconut water as a green and sustainable natural resources. Our results showed that microwave-assisted phosphorylation is an effective way to prepare an electrolyte membrane from nata-de-coco. The synthesis of nata-de-coco and its phosphorylated products has also used cheap and environmentally-friendly chemicals and techniques. At the optimum phosphorylation condition, it can be seen that the proton conductivity of the membrane could reach a value of 1.2×10^{-2} S cm^{-1} and a methanol permeability of 2.3×10^{-6} cm^2 s^{-1}.

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