RESEARCH Revista Mexicana de Física **60** (2014) 249–252 MAY-JUNE 2014

Dependence of the mechanical and electrical properties on the acid content in PVA+H_3PO_2+H_2O membranes

M. E. Fernández[a,*], J.E. Castillo[a,b], F. Bedoya[a,c], J. E. Diosa[a], and R. A. Vargas[a]
[a]*Grupo de Transiciones de Fase en Sistemas no Metálicos, Departamento de Física,*
Universidad del Valle, Calle 13 100-00, A.A. 25360, Cali, Colombia,
e-mail: maria.fernandez.lopez@correounivalle.edu.co
[b]*School of Mechanical Engineering, Purdue University,*
585 Purdue Mall West Lafayette, IN.47907-2088.
[c]*School of Nuclear Engineering, Purdue University,*
400 Central Drive, West Lafayette, IN.47906.

Received 17 May 2013; accepted 25 March 2014

In this paper we report elastic modulus and ionic conductivity measurements in proton-exchange membranes based on poly (vinyl alcohol) (PVA), as a function of the acid (H_3PO_2) concentration and temperature. Tensile stress-strain test (nominal stress) was performed at low rate deformation, with acid concentration between 0.0 to 3.0 given in P/OH ratios. Results show that the elastic modulus, the elastoplastic modulus and the yield stress decrease as acid concentration increases. Ionic conductivity was obtained using the impedance spectroscopy technique on samples with the same acid concentrations, which shows an improvement in ionic conductivity of PVA+H_3PO_2+H_2O within the range 10^{-3} - 10^{-1} S cm^{-1} as the acid concentration increases. The results obtained by comparing mechanical and electric properties, show that they are both directly linked to the acid content and water activity, thus these properties can be engineered to meet the appropriate conditions for an efficient fuel cell operation.

Keywords: Elastic modulus; stress; impedance spectroscopy; dc conductivity; polymer electrolyte.

En este trabajo reportamos medidas del módulo elástico y conductividad iónica en membranas intercambiadoras de protones basadas en alcohol polivinílico (PVA) y ácido hipofosforoso (H_3PO_2). Estas medidas se realizaron como función de la concentración de ácido y la temperatura. Las pruebas de esfuerzo de fluencia se realizaron para las relaciones P/OH: 0.0 a 3.0 a una baja velocidad de deformación. Los resultados muestran que el módulo elástico, el módulo elastoplástico y la tensión de fluencia decrecen al aumentar la concentración de ácido. Las medidas de conductividad iónica, se obtuvieron por espectroscopía de impedancia, para muestras con las mismas relaciones P/OH, las cuales muestran que la conductividad mejora en un rango entre 10^{-3} - 10^{-1} S cm^{-1} con el incremento del ácido. Los resultados obtenidos al comparar las propiedades mecánicas y eléctricas muestran que ambas están directamente relacionados con el contenido de ácido y la actividad del agua, por lo tanto presentan propiedades adecuadas para operación en celdas de combustible.

Descriptores: Modulo elástico; esfuerzo; espectroscopía de impedancia; conductividad dc; electrolito polimérico.

PACS: 62.20.F; 62.40.+i; 82.47.Nj

1. Introduction

Since 1999 when proton conductive membranes based on PVA and hypophosfhorous acid were synthesized [1], great interest in this system appeared due to its excellent ionic conductivity at room temperature (above 10^{-1} S cm^{-1} for higher acid concentration samples) and good thermal stability in the same range of temperatures in which PEM fuel cells work (30-100°C) [2,3].

In this water-swollen polymer electrolyte, liquid-phase electrolyte solution is embedded in a polymer matrix and ionic motion takes place mainly in the liquid phase of the complex. Ionic conductivity is not linked to the polymer dynamics and high conductivities can be observed even below the glass transition temperature of the polymer (T_g) and the temperature dependence of conductivity can be described by the Arrhenius-type equation, $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ where k is the Boltzmann's constant, E_a is the activation energy, σ_0 is the preexponential factor.

Water content and acid concentration improves ionic conductivity significantly, however, they both cause the mechanical stability to decrease, which depends on the microstructure of the membrane altered by its acid content, such as: the degree of crystallinity, degree of crosslinking, plasticizing and biphasic character [4-6]. In this work we studied acid concentration effect on electrical and mechanical properties in PVA+H_3PO_2+H_2O system, by using complex impedance techniques and tensile stress-strain tests in all the concentration range mentioned above.

2. Experimental

2.1. Sample Preparation

We used 98% -99% hydrolyzed PVA (Aldrich), with molecular weight between 85.000 to 146.000, and H_3PO_2 in aqueous solution 50 wt. % (Aldrich) as chemicals precursors. The PVAL was poured in deionized water and the mixture was put on a heater-magnetic stirrer for one hour at 120°C. Once the polymer was dissolved the heater was turned off and adequate amount of acid was added for each concentration. After two hours of continuous agitation, the mixtures were poured into molds, which were stored in a silica-gel desiccator for several days until they became solid. Membranes with thickness between 0.09 mm and 0.30 mm were removed manually from the molds. Four different concentrations were prepared using a molar ratio P/OH (No. of moles of H_3PO_2 / No. of moles of C_2H_4O), in order to establish the corresponding relationship between the acid phosphate and the hydroxyl groups of the polymer. We prepared four H_3PO_2/PVA concentrations, *e.g.*, P/OH = 0.75, 1.50, 2.25 and 3.00 (In this paper such concentrations are designated as sample 0 for the PVA dissolved in water, and 1, 2, 3 and 4, for the increasing acid concentration respectively).

2.2. Electrical conductivity measurements

The electrical properties of the membranes were analyzed using impedance spectroscopy. The impedance spectra were taken in the frequency range from 25 Hz to 5 MHz, using a LCR meter (Wayne Kerr 6420) controlled by a computer at an excitation signal of 500 mV. Possible nonlinear effects were checked at amplitudes up to 1.0 V over the entire frequency range for a typical cell of two-electrodes configuration, Pt/membrane/Pt. No significant differences in the impedance spectra were observed. The measuring cell was located in a sealed, home-made temperature controlled chamber. An E-type thermocouple located close to the PVA polymer membrane was used for temperature measurements. The impedance data were also recorded for a set of membranes which were previously thermally treated at 100°C for 10 min. Each sample was equilibrated at the experimental temperature for at least 2 min before measurement. The impedance spectrum of the membranes was recorded at various isotherms in the temperature range between 30 and 150°C. The experimental temperatures were maintained within ±0.5°C, under a constant atmosphere of dry air with a relative humidity of 15%.

The dc conductivity was calculated from the Nyquist plots, (-ImZ, ReZ). Due to the high conductivity of the samples tested, all recorded spectra showed two well defined regions: a long tail at low frequencies followed by an arc in the high frequency limit. As a consequence, the bulk resistances of the samples, R, were obtained from the intercept of the low frequency tail of the spectra with the real axis, and using the formula σ = d/AR, where d is the thickness and A is the contact area of the sample.

2.3. Stress-strain measurements

The stress-strain tests were performed using an Instron 3366 universal machine. The specimens were cut according to ASTM D882 norm [9] in rectangular strips with 10 mm wide and 150 mm long, the strips were fixed to 2713-001 Instron jaws specially designed for sheets test, minimizing stress concentration effects at the edges of the sample. Tensile test of all samples were conducted at room temperature (T=23°C) with a constant strain rate of 10 mm/min and under an atmosphere at 66% relative humidity.

3. Results and Discussion

Figure 1(a) shows the temperature dependence of the dc ionic conductivity for the raw samples. Based on least square analysis of the corresponding data, straight lines fit well all Arrhenius plots, $\log\sigma$ vs. T^{-1}, if a low temperature segment of each data plot is selected: from 30 to 70°C for samples 1 and 2, from 30 to 80°C for sample 3, and from 30 to 100°C for sample 4. Upper limit of each range marks the onset temperature at which water content into the membranes are no longer at equilibrium with the surrounding atmosphere and starts to diffuse out of the membrane, leading to a decrease in conductivity [1-3].

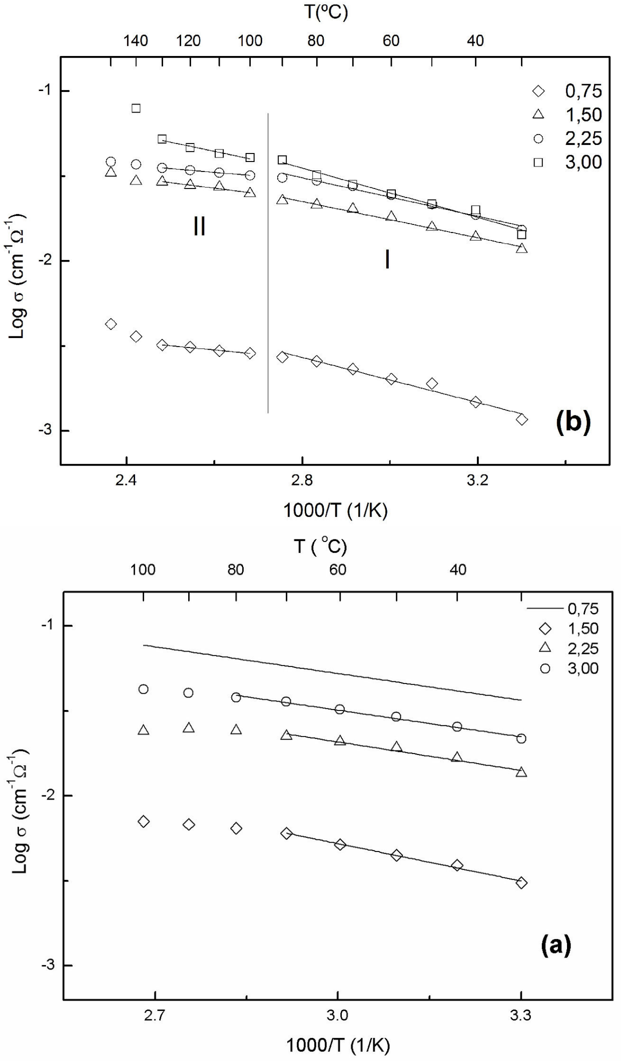

FIGURE 1. Log conductivity vs reciprocal temperature for: (a) raw samples, (b) heat-treated samples.

TABLE I. Activation energy for raw and heat treated samples as calculated to the linear fitting to Eq. (1)

	E_a (eV)		
	Raw	Heat treated samples	
P/OH	samples	Region I	Region II
0.75	0.14	0.13	0.05
1.50	0.11	0.11	0.06
2.25	0.10	0.11	0.04
3.00	0.10	0.14	0.11

Figure 1(b) shows the Arrhenius plots of the dc conductivity data for thermally treated samples in which two linear trends are observed. In the first region between 30°C and 90°C, the data could be fitted with straight lines over the entire range because the effect of water loss was not significant. Above 90°C ionic conductivity has a lower thermal activation and linear fittings could be made up to 130°C where divergences from the linear behavior are observed, probably due to softening of the PVA matrix

The activation energies (Ea) presented in Table I were obtained as fitting parameters using the Arrhenius model,

$$\log\sigma = \log\sigma_0 - E_a/kT\,. \tag{1}$$

Note that E_a decreases slightly with increasing acid concentration for raw samples, *e.g.*, from 0.14 to 0.10 eV. For heat treated samples, they show activation energies comparable to those of the first set of samples, but they did not show the same trend as a function of the acid content. In region II the abrupt decrease of the activation energy, indicates that the conduction process is less sensitive to increases in temperatures above 90°C.

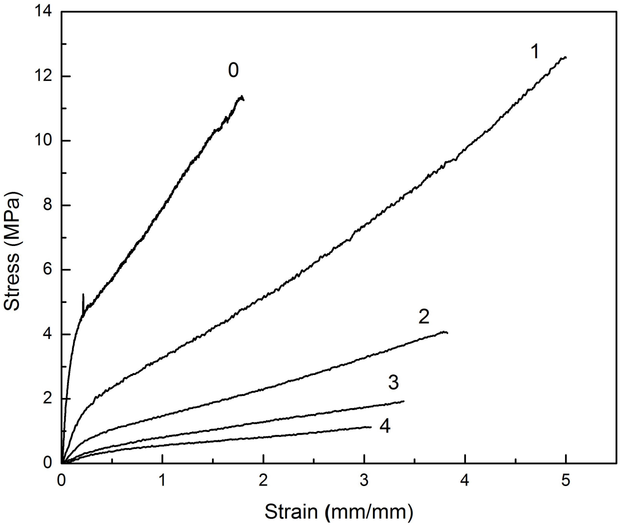

FIGURE 3. Stress vs strain curves for the samples 0, 1, 2, 3, 4, 5 at constant strain rate (10 mm/min).

Figure 2 shows the stress-strain curves of the membrane with concentration P/OH: 0.75, obtained at room temperature. The modulus (E) was calculated from the slope of the stress (σ)-strain (ε) curve ($E = \partial\sigma/\partial\varepsilon$). Two linear regions are observed with increasing strain. The elastic or Young's modulus was calculated as the slope of the first linear region, and the elastoplastic modulus corresponding to the slope of the second linear region [10]. Because this type of response has no well defined yield point, different authors have estimated a "proportional limit" as the value of the stress in which these two lines intersect [7-8].

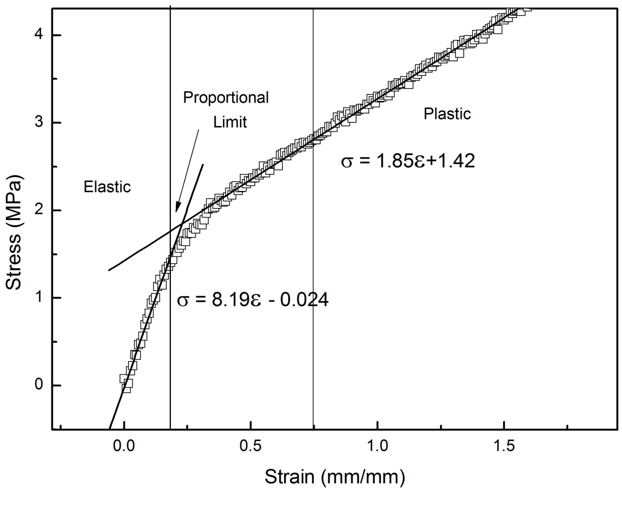

FIGURE 2. Stress-strain curve for the sample P/OH: 0.75.

Figure 3 shows the stress-strain curves of membranes with all the concentration prepared, obtained at room temperature. It is evident that exist a marked decrease in the toughness of the samples as the acid concentration increases. The obvious trend is that the initial slope, which is the elastic modulus, decreases with increasing acid content (*i.e.* the membranes become less stiff with increasing acid concentration). Moreover, the proportional limit appears to decrease with increasing acid content. It is also evident in Fig. 3 that increasing acid concentration reduces the elastic deformation zone.

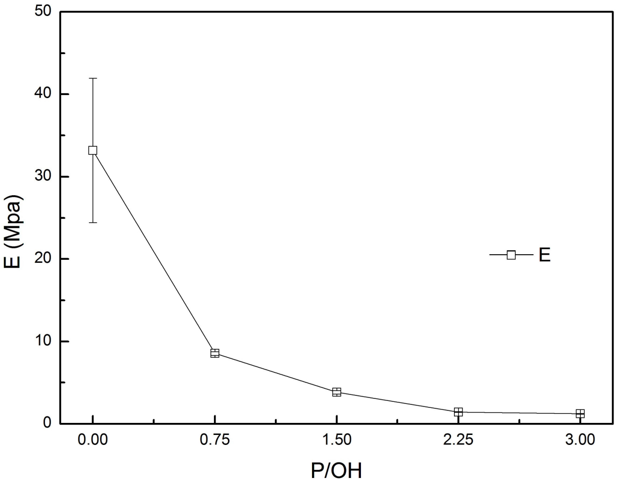

FIGURE 4. Elastic modulus vs concentration P/OH, for raw samples.

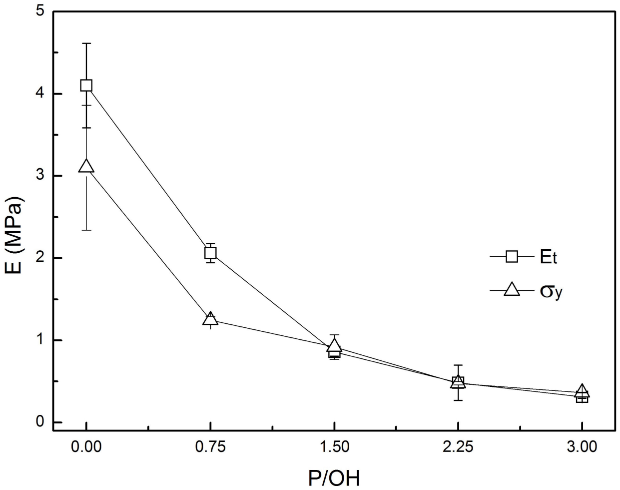

FIGURE 5. Elastoplastic modulus (E_t) and proportional limit (σ_y) vs P/OH concentration, for raw samples.

As the acid concentration in the membranes increases, the elongation at break decreases, thus indicating that polymer chain interactions become weaker. This may be so because the interaction of the hydroxyl groups attached to the polymer backbone with neighboring polymer's chains, which play an important role in the rigidity of PVA [5,10,11], decreases with acid concentration into the polymer matrix [4]. In pure PVA and under dry conditions, the dipole interactions among neighboring OH groups bind the polymer chains together. By increasing the amount of acid into the clusters of the polymer matrix, the binding energy between the polymer chains decreases. In other words, the acid dilutes the polymer chains interaction.

Figures 4 and 5 summarize the stress-strain test for the membranes with increasing acid concentration prepared at room temperature. Figure 4 shows the elastic modulus (E) and Fig. 5 displays both the elastoplastic modulus (E_t) and the proportional limit stress (σ_y) of the membranes plotted as function of P/OH concentration ratio. They all appeared to decrease rapidly in tandem with the acid content.

4. Conclusions

Conductivity for the fully hydrated PVA+H_3PO_2+H_2O polymeric system decreases about half order of magnitude when they are dehydrated. In dehydrated samples the ionic conductivity shows no appreciable change with increasing acid concentration above P/OH=0.75, while in raw sample the conductivity increases rapidly with increasing P/OH ratios up to 10^{-1} Scm^{-1} at 100°C for P/OH=0.30.

Using linear fittings to the stress-strain data recorded at room temperature for hydrated membranes, the Young's modulus, yield stress and ultimate stress were obtained, and plotted as a function of P/OH concentration, showing a clear decreasing trend with increasing acid content.

Thus, in this acid-based polymer electrolyte, as the acid content increases, the ionic conductivity increases significantly; nonetheless, it has a negative effect in the mechanical properties. The mechanical behavior of these membranes clearly suggests that they can be modeled as a superposition of an elastic solid and a vicious fluid.

In summary, our findings indicate that the mechanical and proton transport properties of the membranes are both directly linked to a two-phase structure, where liquid-like H_3PO_2/H_2O clusters expand with increasing acid content, whereas the solid-like polymer backbone maintains the structural stability. The membranes become less stiff with increasing acid concentration.

Acknowledgments

The authors are grateful for financial support from the Colombian Funding Agency (COLCIENCIAS) and the Center of Excellence in New Materials (CENM), Universidad del Valle, Cali, Colombia.

---

1. M.A. Vargas, R.A. Vargas, and B.E. Mellander, *Electrochim. Acta* **44** (1999) 4227.
2. M.A. Vargas, R.A. Vargas, and B.E. Mellander, *Electrochim. Acta* **45** (2000) 1399.
3. R.A. Vargas, V.H. Zapata, E. Matallana, and M.A. Vargas, *Electrochimica Acta* **46** (2001) 1699.
4. P.N. Gupta and K.P. Singh, *Solid State Ionics* **86-8** (1996) 319.
5. M. L. Cerrada Garcia, Ph. D. thesis, Universidad Complutense de Madrid, 1995. http://biblioteca.ucm.es/tesis/19911996/X/0/X0034101.pdf
6. Y. Tang, A. M. Karlson, M. H. Santare, M. Gilbert, S. Cleghorn, and W. B. Johnson, *Mater. Sci. Eng. A* **425** (2006) 297.
7. M. Barclay Satterfield, P. W. Majsztrik, H. Ota, J. B. Benziger, and A. B. Bocarsly, *J. Poly. Sci. Part B.* **44** (2006) 2327.
8. Y. Tang, A. Kusolu, A. M. Karlson, M. H. Santare, S. Cleghorn, and W. B. Johnson, *J. Power Sources* **175** (2008) 817.
9. American Society of Testing Materials. Standard Test Method for Tensile Properties of Thin Plastic Sheeting. (ASTM, 2009). p. 10 (ASTM D882-09)
10. M.H Yu, *Generalized Plasticity* (Springer, Berlin, 2006) p.122.
11. L. E. Nielsen and R. F Landen, *Mechanical Properties of Polymers and composites* (Marcel Dekker Inc., New York, 1994) p.135.