Vol. 21, n.°4, pp. 63-70, 2022
Revista UIS Ingenierías
Página de la revista: https://revistas.uis.edu.co/index.php/revistauisingenierias

Study of the humidity effect on the mechanical properties of $PVOH+H_3PO_2/TiO_2$ proton exchange membranes

Estudio del efecto de la humedad sobre las propiedades mecánicas de membranas de intercambio protónico de $PVOH+H_3PO_2/TiO_2$

Nadia Combarizao [1], Jesus Evelio Diosa-Astaiza[2a, 3], Diego Peña-Lara [2b, 3]

[1] SDG nexus Network, Justus-Liebig-Universität Giessen (JLU Giessen), Germany. Email: Nadia.Combariza@zeu.uni-giessen.de Orcid: 0000-0002-4109-8695
[2] Grupo de Transiciones de Fase y Materiales Funcionales, Departamento de Física, Universidad del Valle, Colombia. Emails: jesus.diosa@correounivalle.edu.co [a], diego.pena@correounivalle.edu.co [b], Orcid: 0000-0002-1919-1922 [a] , 0000-0001-6199-1547 [b]
[3] Centro de Excelencia en Nuevos Materiales, Universidad del Valle, Colombia.

Received: 25 July 2022. Accepted: 12 September 2022. Final version: 31 October 2022.

Abstract

The elastic modulus of polymeric membranes based on PVOH + H_3PO_2 + TiO_2 was studied as a function of relative humidity (%RH) and the volumetric fraction of water. Tensile stress-strain tests (nominal stress) were performed to determine Young's modulus, yield strength, break stress, and strain stress at a constant speed of 10 mm/min. The membrane’s acid concentration was kept constant at the molar concentration of high proton conduction P/OH = 0.3, and they were separated into two test groups, 5 wt. %TiO_2 fillers, and without TiO_2. For relative humidity between 8 and 94% RH, the membranes with TiO_2 show an improvement in the elastic modulus concerning those without TiO_2 doping, but they have no significant difference at 100% RH, under a confidence level of 95%. In general, the data analysis indicates that the mechanical properties and the electrical properties of the membranes previously reported are directly related to the absorption of water contained in the hydrophilic groups that expand during swelling. In contrast, the hydrophobic solid-like polymer backbone and the TiO_2 nanoparticle fillers maintain structural stability.

Keywords: elastic modulus; stress; polymeric composites.

Resumen

Se estudió el módulo de elasticidad de membranas poliméricas a base de PVOH + H_3PO_2 + TiO_2 en función de la humedad relativa (%HR) y la fracción volumétrica de agua. Se realizaron ensayos de tensión-deformación por tracción (tensión nominal) para determinar el módulo de Young, límite elástico, tensión de rotura y tensión de deformación a una velocidad constante de 10 mm/min. La concentración de ácido de las membranas se mantuvo constante a la concentración molar de alta conducción de protones P/OH = 0.3 y se separaron en dos grupos de prueba, con dopado del 5 wt. % TiO_2 y sin TiO_2. Para humedades relativas entre 8 y 94% HR, las membranas con TiO_2 muestran una mejora en el módulo elástico con respecto a aquellas sin dopado de TiO_2, pero no tienen diferencia significativa a 100% HR, bajo un nivel de confianza del 95%. En general, el análisis de los datos indica que las propiedades

ISSN Printed: 1657 - 4583, ISSN Online: 2145 - 8456.

How to cite: N. Combarizao, J. E. Diosa-Astaiza, J. B. Cano-Quintero, “Study of the humidity effect on the mechanical properties of PVOH+H3PO2/TiO2 proton exchange membranes,” *Rev. UIS Ing.*, vol. 21, no. 4, pp. 63-70, 2022, doi: https://doi.org/10.18273/revuin.v21n4-2022006.

mecánicas, así como las propiedades eléctricas de las membranas reportadas previamente, están directamente relacionadas con la absorción de agua contenida en los grupos hidrofílicos que se expanden durante el incremento de volumen del polímero, mientras que la columna vertebral del polímero hidrofóbico, similar a un sólido, y las nanopartículas de TiO_2 mantienen la estabilidad estructural.

Palabras clave: módulo elástico; tensión; compuestos poliméricos.

1. Introducción

The polymer electrolyte membrane in a fuel cell (PEMFC) is responsible for proton conduction from the anode to the cathode while acting as an electron's insulator and as a gas barrier to avoid the mixture of oxygen with hydrogen [1]. Those fuel cells operate in a wide range of temperatures and humidity [2]; during normal operation, due to the entrance of gases, the membrane environmental conditions constantly change in a humidity cycle [3]. The membrane undergoes expansion and contractions as a function of temperature and humidity [1], which is one of the main consequences of the damage and eventual malfunction of the fuel cell [3].

The water content in the membrane is an essential factor in increasing ion conductivity [4], [5], [6]. However, excess water absorption usually results in a higher degree of membrane swelling, which leads to a decrease in mechanical properties [4], [5], [7].

PVOH has proven to be an excellent low-cost polymer for developing proton exchange membranes [8], [9], [10], [11], [12], [13], [14]. The observation of high-proton conductivity in acid-doped PVOH membranes has opened up the possibility of using these polymers in solid-state ionic devices. Furthermore, doping with salts, acids, or inert micro or nanoparticles (TiO_2, Al_2O_3, ZrO_2, SiO_2) have shown changes in their electrical, thermal, and mechanical properties [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23]. In this work, we studied water concentration and the nanoparticles fillers' effect, on the mechanical properties in the PVOH + H_3PO_2 + TiO_2 system, by performing tensile stress-strain tests in all the concentration ranges mentioned above.

2. Experimental

2.1. Preparation of membrane samples

Hydrolyzed (98%−99%) poly (vinyl alcohol) (Aldrich-363154), with molecular weight between 85000-146000; hypophosphorous acid (H3PO2), 50% concentration in aqueous solution (CAS 6883-21-5) (Carlos Erba); and titanium oxide nanopowder (Aldrich-634662), were used.

Constant polymer amounts were mixed with deionized water using a magnetic stirrer at 120 °C for 2 hours until the mixture became homogeneous and all polymer grains dissolved. Then, maintaining the mixture under agitation, constant amounts of acid were added to the solution, according to the molar ratio P/OH = 0.3. After additional two hours under agitation, the mixture, now at room temperature, was poured into glass vessels under a dry atmosphere for several days to obtain membranes. The resulting membranes were uniform, smooth, thin (thickness between 90 and 300 µm), and semi-transparent to visible light.

The second group of membranes with 5 wt. % of TiO_2 was prepared similarly to that described above. However, the appropriate weight ratio of TiO_2 nanoparticles was added to the P/OH = 0.3 solutions, which was stirred continuously until the mixture became homogeneous viscous.

2.2. Experimental apparatus

The stress-strain test was performed using a modified device, based on a Com Ten Universal Test stand, controlled by a computer using a LabView® platform. The program generates a stress-strain graphic from the force-displacement data recorded during the tensile testing using the nominal dimensions (thickness, width, and grip separation) and the strain rate. The test conditions were made under the ASTM- D882 norm.

To calculate the equivalent dry weight of the membrane, thermogravimetric analysis (TGA) was performed using a TA Instruments 2050 TGA microbalance controlled by a computer.

2.3. Testing procedures

The membranes were cut into rectangular films of 10.0 mm in width and 50.0 mm in length. Tensile stress-strain of the membranes with the concentration prepared was measured as a function of relative humidity and water content. The tensile test was conducted at room temperature (T = 27°C) with a constant strain rate of 10 mm/min and a 30 mm grip separation.

Three membranes for each group were tested (with and without nanoparticles) at 8 pre-equilibrated humidity conditions. To vary those parameters, membranes were conditioned over saturated salt solutions, acid and water contained in tight- sealed flasks: H_2SO_4 (5% RH), $CaCl_2$ (30% RH), ambient conditions (~57% RH), $CaCl_2$ + H_2O (66% RH), NaCl (72% RH), $(NH_4)_2SO_4$ (77% RH), K_2SO_4 (94% RH) and H_2O (~100% RH). The relative humidity in every environmental chamber was measured using an Omega-60 sensor.

After 2 weeks, one membrane was selected randomly, removed from the controlled humidity, and tested under ambient conditions of (27−30 °C and 57−61% RH). Testing was completed in ~3 min, membranes were weighed before and after the test, and its mean value was taken as the hydrated weight. For each membrane, the thickness and width were measured with a micrometer and a caliper, respectively, at three locations along the sample before testing, and the averages of these three measurements were used as the nominal dimensions of the sample.

The equivalent dry weight of each membrane was calculated using thermogravimetric analysis (TGA). A sample from each group (with and without nanoparticles) was initially heated from room temperature to 115 °C to remove the superficial water, and then it was heated from 95 °C to 260 °C, at a rate of 10 °C/min, using dry nitrogen as a purge gas. The weight percentage was determined when the sample was dry. This value was used to calculate the equivalent dry weight of each membrane as a percentage of its weight at ambient conditions.

3. Results and discussion

3.1. Stress-strain response at different humidity

Figure 1 shows the typical viscoelastic stress-strain results for membranes at 8 different atmospheres prepared without TiO_2 nanoparticles and with a concentration of 5% TiO_2 nanoparticles. Two linear regions are observed; the first zone corresponds to elastic deformation, and the second zone is associated with elastoplastic deformation. The membranes did not present a failure during the testing. As humidity increases, the tensile strength decreases and affects mechanical stability.

The elastic modulus results are plotted as a function of humidity in Figure 2.

An analysis of variance was done to determine if the influence of humidity was significant between the two groups of membranes. A two factors model was used; the first factor is the atmosphere, which has 8 levels representing each relative humidity controlled in the experiment, and the second level is the use of nanoparticles with two levels, with 5% TiO_2 and without them. Consequently, the following expression is proposed for the data analysis of the elastic modulus:

$$y_{ijk} = \mu_i + \tau_j + \beta_k + (\tau_j \beta_k) + \varepsilon_{ijk} \qquad (1)$$

where y_{ijk} is the measured value, μ_i is the overall effect associated with the mean value of all the results, τ_j, and β_k represents the effects of the atmosphere and the use of nanoparticles, respectively, $(\tau_j \beta_k)$ is the effect of the interaction atmosphere-nanoparticles, and ε_{ijk} is the effect of the uncontrolled variables.

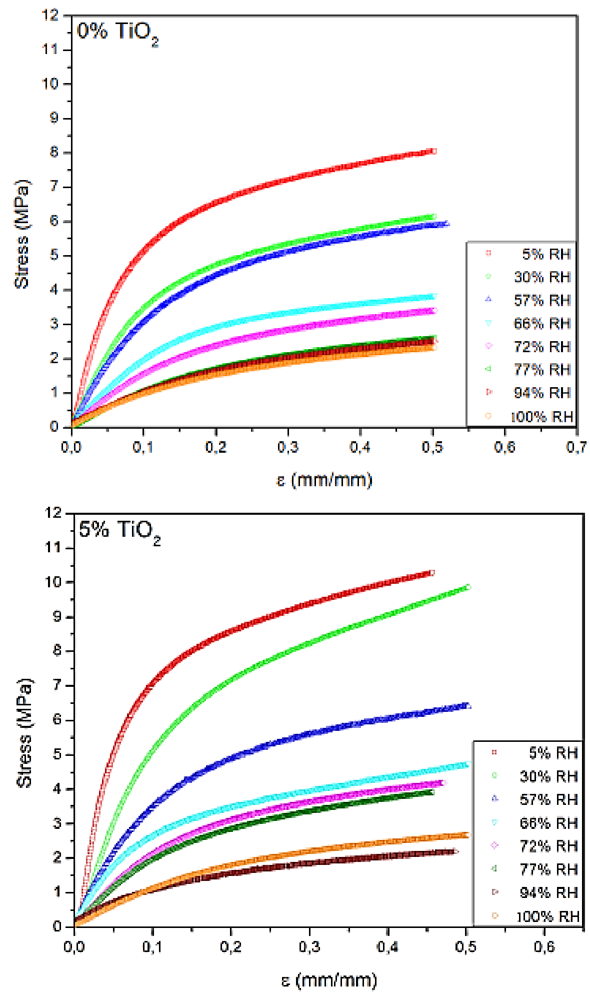

Figure 1. Stress-strain curves for the P/OH = 0.3 molar ratio membranes without and with dispersing 5% TiO2 nanoparticles at 27 °C as a function of relative humidity.

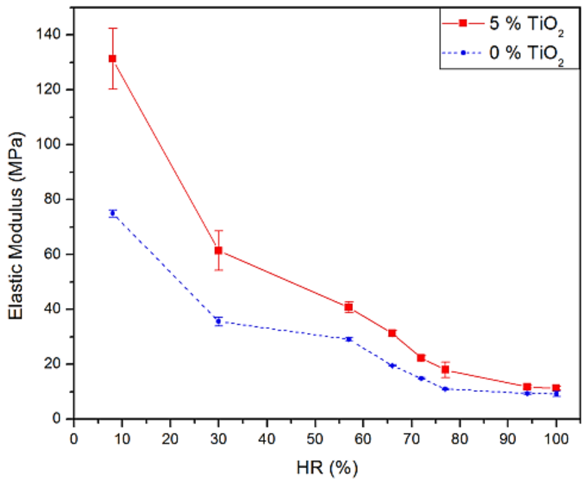

Figure 2. Elastic modulus of the P/OH = 0.3 molar ratio membranes with and without dispersing 5% TiO_2 nanoparticles, at 27 °C, as a function of relative humidity.

An analysis of variance was done to determine if the influence of humidity was significant between the two groups of membranes. A two factors model was used; the first factor is the atmosphere, which has 8 levels representing each relative humidity controlled in the experiment, and the second level is the use of nanoparticles with two levels, with 5% TiO_2 and without them. Consequently, the following expression is proposed for the data analysis of the elastic modulus:

$$y_{ijk} = \mu_i + \tau_j + \beta_k + (\tau_j \beta_k) + \varepsilon_{ijk} \qquad (1)$$

where y_{ijk} is the measured value, μ_i is the overall effect associated with the mean value of all the results, τ_j, and β_k represents the effects of the atmosphere and the use of nanoparticles, respectively, $(\tau_j \beta_k)$ is the effect of the interaction atmosphere-nanoparticles, and ε_{ijk} is the effect of the uncontrolled variables.

Using the elastic modulus as our measured value, the assumption of normality did not meet under a confidence level of 95%.; therefore, it was necessary to do a transformation of variance, resulting in the logarithm function, log (y_{ijk}), being the most appropriate one.

The result of the variance analysis was that the fundamental factors and their interaction among them have a significant effect on the result (i.e., $p \leq 0.001$). For that reason, Tukey's significant test was done to determine if there was a significant difference between the mean values for each factor level.

The results of Tukey's analysis for the atmospheres show a significant difference between the results of log (y_{ijk}), for RH < 94%. For atmospheres with relative humidity between 94 and 100% RH (K_2SO_4 and H_2O, respectively) the value of p is superior to 0.05. It means that under a confidence level of 95%, there was no significant difference between the values of log (elastic modulus).

An additional Tukey's analysis was done to check the influence of using nanoparticles in log (elastic modulus), leading to the conclusion that a 5% TiO_2 concentration has a relevant effect. Moreover, performing a variance analysis in which each atmosphere was considered separately such that it resulted in a one-factor model (that of the nanoparticles) for log (elastic modulus), the value of p was bigger than 0.05 at the water atmosphere (~100% RH). It is then confirmed that with membranes with nanoparticles in a concentration of 5% TiO_2 under an atmosphere with RH > 94%, there is no significant difference in the log value (elastic modulus).

3.2. Thermal characterization: TGA results

Samples' weight loss as a function of temperature after being thermally pretreated as described above is depicted in Figure 3. The thin line corresponds to the derivative of the weight loss. It can be seen that, even though the polymer degradation peak for both samples appears at approximately the same temperature (at about 225 °C), the sample without nanoparticles has a higher rate of weight loss. Based on Figure 3, the dry membrane weight without nanoparticles is about 77.5%, while that of the membranes with 5% TiO_2 is about 84% of their initial weights at room temperature.

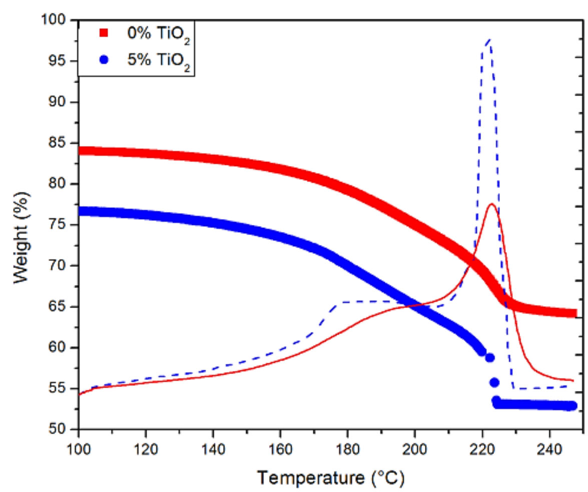

Figure 3. TGA curves for the studied concentration as a function of temperature.

A second TGA curve was done to find if the membranes with 5% TiO_2 can retain water for a more extended time under an isotherm at 30 °C. In Figure 4, we can observe that both curves level off at about the same time (approximately 60 min), but the sample with titanium oxide nanoparticles can retain water better than the sample without nanoparticles. The initial rapid weight loss is attributed to surface water evaporation under a dry nitrogen atmosphere.

The TGA results then show the positive effect of nanoparticle addition to the studied membranes on their water uptake capacity.

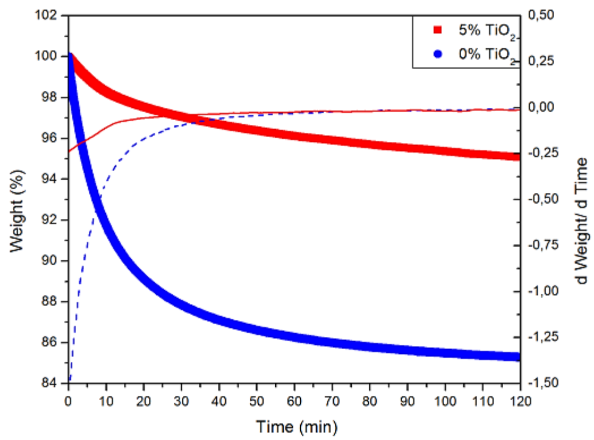

Figure 4. TGA curves for the studied concentrations as function of time.

3.3. Water volume fraction at different humidity

The water volume fraction was calculated using the expression

$$\phi_w = \frac{\Delta V_w}{V_{total}} = \frac{\Delta V_w}{V_p + \Delta V_w + V_{H_3PO_2} + V_{TiO_2}} = \left[1 + \frac{(W_{H_3PO_2}/\rho_{H_3PO_2}) + (W_p/\rho_p) + (W_{TiO_2}/\rho_{TiO_2})}{((W_p{}^{swollen} - W_p{}^{dry})/\rho_w)}\right]^{-1} \quad (2)$$

where $(W_p{}^{swollen} - W_p{}^{dry})$ is the mass gained by the membrane concerning that of the dry state due to the water uptake at each controlled atmosphere; $W_{H_3PO_2}$, W_p and W_{TiO_2} are the mass fraction of hypophosphorous acid, dry polymer and titanium oxide in the membrane, respectively, and $\rho_{H_3PO_2}$, ρ_p, ρ_{TiO_2} and ρ_w are the corresponding mass density.

The water volume fraction of the membranes as a function of humidity is depicted in Figure 5.

An analysis of variance was done to determine if the influence of humidity was significant between the two groups of membranes concerning the water volume fraction. The factors and their interaction significantly affect the result ($p \leq 0.001$). A two factors model was then used in Eq. (1). In this case, the water volume fraction, as the measured value, meets the normality assumption under a confidence level of 95%.

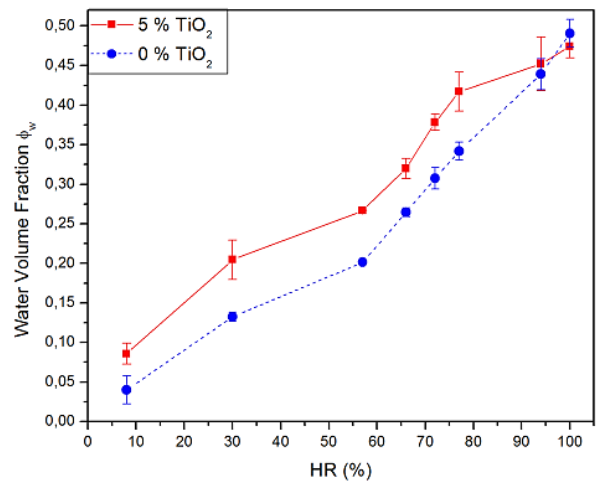

Figure 5. Water volume fraction for the studied concentration as a function of relative humidity.

Tukey's significant test was also done to analyze the various factors that affect the water volume fraction as a function of the relative humidity of the surrounding atmosphere. The results of Tukey's analysis for the significant difference in the water volume fraction due to each atmosphere that is for NaCl (72% RH), $(NH_4)_2SO_4$ (77% RH), K_2SO_4 (94% RH), and H_2O (~100% RH), have a p-value bigger than 0.05, so for this atmosphere, the corresponding water volume fraction for each pair is not significantly different using a confidence level of 95%.

On the other hand, the result of Tukey's analysis for the influence of using nanoparticles on the water volume fraction shows that a 5% TiO_2 concentration has a relevant effect on the value of log(elastic modulus). A variance analysis was also done on each atmosphere using a factor model, where the factor was the use of nanoparticles. The value of p was higher than 0.05 at the H_2SO_4 (5% RH), K_2SO_4 (94% RH), and H_2O (~100% RH) atmospheres. The mass gained by the membranes at those atmospheres is approximately the same for the membranes with and without nanoparticles. However, when the relative humidity is near room conditions, the weight change is clearly distinguished between the membranes with and without nanoparticles.

Figure 5 shows the calculated water volume fraction, ϕ_w, as a function of the relative humidity, RH (%), we can observe that the two curves intersect at a relative humidity between 94 and ~100%. In the variance analysis of the log (elastic modulus) using a two factors model, it was found that at these two atmospheres, the log elastic modulus does not change significantly; however, there is a water volume fraction change; therefore, it can be inferred that the weight change is due to free water.

3.4. Elastic Modulus as a function of water volume fraction

Figure 6 shows the elastic modulus as a function of the polymer volume fraction. The polymer volume fraction is the complement of the water volume fraction ($\phi_p = 1 - \phi_w$). It is observed that even when the two groups of membranes were in the same atmospheres, the tendency of their elastic modulus is different, as was inferred from the variance analysis, where the interaction atmosphere-nanoparticles presented significant differences.

A power-law relationship given by Equation (3) describes well the experimental results as the fitting curves shown in Figure 6,

$$E_E = A + B{\phi_p}^{\alpha} \tag{3}$$

The fitting parameters to Equation (3) are listed in Table 1. $E_E{}^{dry}$ is the elastic modulus of the dry membrane at $\phi_p = 1$.

4. Conclusions

Tensile stress-strain properties of the P/OH = 0.3 molar ratio membranes with and without dispersing 5% TiO_2 nanoparticles have been measured at 27°C and 0−100% relative humidity. In general, the elastic modulus of the membranes with the concentration prepared decreases with increasing the surrounding atmosphere's relative humidity.

According to the statistical variance analysis of the experimental data, at the highest humidity atmospheres (≥ 94% RH), the elastic modulus does not have significant changes. Since there are changes in the water volume fraction, and this calculation is based on the weight change of the membrane, the result suggests that these changes are due to free water.

The TGA curves show evidence that membranes with nanoparticles in a concentration of 5% TiO_2 retain water for a longer time compared to those without nanoparticles. On the other hand, the results of the uniaxial tensile test at room temperature indicate that at atmospheres between 8 and 94% RH, nanoparticles reinforce the membranes leading to the higher elastic modulus. These values are pretty separated between the two groups of membranes under atmospheres at low humidity; however, in atmospheres at high humidities, elastic modulus values for membranes with 5% TiO_2 are closer to those values in membranes without nanoparticles.

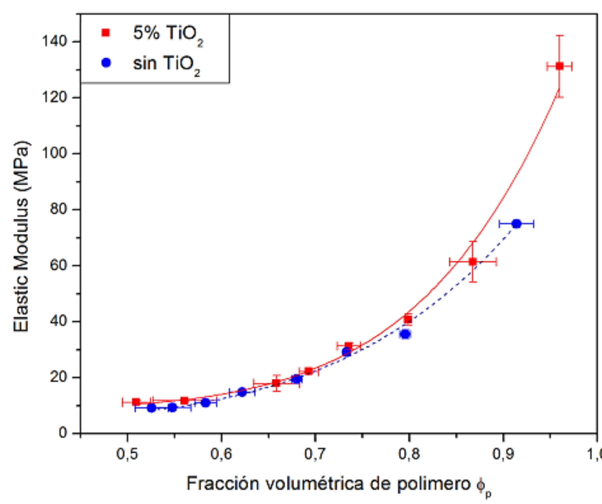

Figure 6. The elastic modulus for the studied concentration as a function of the polymer volume fraction. Solid lines are the fittings curves to Eq. (3).

Table 1. Fitting parameters to Equation (3) for the elastic modulus data as a function of the polymer volume fraction

Curve	$A\ [Mpa]$	$B\ [Mpa]$	α	$E_E{}^{dry}\ [Mpa]$	R^2
0% TiO_2	$3{,}92 \pm 1{,}08$	$111{,}49 \pm 5{,}73$	$5{,}03 \pm\ 0{,}31$	$115{,}41 \pm\ 5{,}73$	99,22 %
5% TiO_2	$8{,}69 \pm 0{,}94$	$150{,}41 \pm 18{,}21$	$6{,}52 \pm\ 0{,}55$	$159{,}10 \pm 18{,}21$	98,01 %

Comparing the mechanical properties with the previous results on the proton transport in the membranes with the concentration prepared as a function of the surrounding atmosphere, relative humidity RH(%), it is inferred that both their electrical and mechanical properties are directly linked to their water uptake contained in the hydrophilic clusters that expand during swelling, whereas the hydrophobic solid-like polymer backbone and the inert nanoparticle fillers maintain the structural stability.

Acknowledgements

The authors thank the support from M. E. Fernandez, J. Angel, J. Castillo, and F. Bedoya, and the Center of Excellence in New Materials (CENM), Universidad del Valle, Cali, Colombia.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reports in this manuscript.

References

[1] Y. Tang, A. M. Karlsson, M. H. Santare, M. Gilbert, S. Cleghorn, W. B. Johnson, "An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane," *Mater. Sci. Eng. A*, vol. 425, no. 1–2, pp. 297–304, 2006, doi: http://doi.org.10.1016/j.msea.2006.03.055

[2] S. Cleghom, W. J. Kolde, "Catalyst coated composite membranes," in *Handbook of Fuel Cells - Fundamentals, Technology and Application*, W. Vielstich, A. Lamm, H. A. Gasteiger, Eds. Chichester: John Wiley & Sons, Ltd, 2003, pp. 566–575.

[3] S. F. Burlatsky et al., "A mathematical model for predicting the life of polymer electrolyte fuel cell membranes subjected to hydration cycling," *J. Power Sources*, vol. 215, pp. 135–144, 2012, doi: http://doi.org.10.1016/j.jpowsour.2012.05.005

[4] A. Kusoglu, A. M. Karlsson, M. H. Santare, "Structure-property relationship in ionomer membranes," *Polymer (Guildf).*, vol. 51, no. 6, pp. 1457–1464, 2010, doi: http://doi.org.10.1016/j.polymer.2010.01.046

[5] S. Bose, T. Kuila, T. X. H. Nguyen, N. H. Kim, K. Lau, J. H. Lee, "Polymer membranes for high temperature proton exchange membrane fuel cell: Recent advances and challenges," *Prog. Polym. Sci*., vol. 36, no. 6, pp. 813–843, 2011, doi: http://doi.org.10.1016/j.progpolymsci.2011.01.003

[6] D. C. Dayton, "Fuel cell integration-a study of the impacts of gas quality and impurities," Golden, CO (United States), 2001.

[7] M. B. Satterfield, J. B. Benziger, "Viscoelastic properties of Nafion at elevated temperature and humidity," *J. Polym. Sci. Part B Polym. Phys*., vol. 47, no. 1, pp. 11–24, 2009, doi: http://doi.org.10.1002/polb.21608

[8] M. Vargas, R. Vargas, B. E. Mellander, "More studies on the PVAl+H3PO2+H2O proton conductor gels," *Electrochim. Acta*, vol. 45, no. 8–9, pp. 1399–1403, 2000, doi: http://doi.org.10.1016/S0013-4686(99)00350-3

[9] I. Palacios, R. Castillo, R. A. Vargas, "Thermal and transport properties of the polymer electrolyte based on poly(vinyl alcohol)–KOH–H2O," *Electrochim. Acta*, vol. 48, no. 14–16, pp. 2195–2199, 2003, doi: http://doi.org.10.1016/S0013-4686(03)00204-4

[10] V. H. Zapata, W. A. Castro, R. A. Vargas, B. E. Mellander, "More studies on the PVOH–LiH2PO4 polymer system," *Electrochim. Acta*, vol. 53, no. 4, pp. 1476–1480, 2007, doi: http://doi.org.10.1016/j.electacta.2007.05.063

[11] W. A. Castro, V. H. Zapata, R. A. Vargas, B. E. Mellander, "Electrical conductivity relaxation in PVOH–LiClO4–Al2O3," *Electrochim. Acta*, vol. 53, no. 4, pp. 1422–1426, 2007, doi: http://doi.org.10.1016/j.electacta.2007.05.066

[12] C. C. Yang, "Synthesis and characterization of the cross-linked PVA/TiO2 composite polymer membrane for alkaline DMFC," *J. Memb. Sci*., vol. 288, no. 1–2, pp. 51–60, 2007, doi: http://doi.org.10.1016/j.memsci.2006.10.048

[13] M. E. Fernández et al., "New polymer electrolyte based on PVAL-LiOH-Al 2 O 3 -H 2 O," *Phys. status solidi c*, vol. 4, no. 11, pp. 4075–4080, doi: http://doi.org.10.1002/pssc.200675934

[14] M. E. Fernándeza, J. E. Castillo, F. Bedoya, J. E. Diosa, R. A. Vargas, “Dependence of the mechanical and electrical properties on the acid content in PVA+H3 PO2 +H2 O membranes,” *Rev. Mex. Física*, vol. 60, pp. 249–252, 2014.

[15] R. A. Vargas, A. García, M. A. Vargas, “Phase behavior of complexes of PVA and acid salts,” *Electrochim. Acta*, vol. 43, no. 10–11, pp. 1271–1274, 1998, doi: http://doi.org.10.1016/S0013-4686(97)10029-9

[16] M. Ali, A. Gherissi, “Synthesis and characterization of the composite material PVA/Chitosan/5% sorbitol with different ratio of chitosan,” *Int. J. Mech. Mechatronics Eng*., vol. 17, pp. 15–28, 2017.

[17] R. P. Gonçalves, W. H. Ferreira, R. F. Gouvêa, C. T. Andrade, “Effect of Chitosan on the Properties of Electrospun Fibers From Mixed Poly(Vinyl Alcohol)/Chitosan Solutions,” *Mater. Res.*, vol. 20, no. 4, pp. 984–993, 2017, doi: http://doi.org.10.1590/1980-5373-mr-2016-0618

[18] S. Aziz, O. Abdullah, S. Hussein, H. Ahmed, “Effect of PVA Blending on Structural and Ion Transport Properties of CS:AgNt-Based Polymer Electrolyte Membrane,” *Polymers (Basel)*, vol. 9, no. 11, p. 622, 2017, doi: http://doi.org.10.3390/polym9110622

[19] M. Benítez, J. E. Diosa, R. A. Vargas, “Effect of H3PO2 on the mechanical, thermal, and electrical properties of polymers based on poly (vinyl alcohol) (PVA) and chitosan (CS),” *Ionics (Kiel)*, vol. 24, no. 7, pp. 2029–2034, 2018, doi: http://doi.org.10.1007/s11581-018-2465-y

[20] D. A. Quintana, E. Baca, E. Mosquera, R. A. Vargas, J. E. Diosa, “Improving the ionic conductivity in nanostructured membranes based on poly(vinyl alcohol) (PVA), chitosan (CS), phosphoric acid (H3PO4), and niobium oxide (Nb2O5),” *Ionics (Kiel)*, vol. 25, no. 3, pp. 1131–1136, 2019, doi: http://doi.org.10.1007/s11581-018-2764-3 .

[21] E. E. Ruiz Gómez, J. H. Mina Hernández, J. E. Diosa Astaiza, “Development of a Chitosan/PVA/TiO2 Nanocomposite for Application as a Solid Polymeric Electrolyte in Fuel Cells,” *Polymers (Basel)*, vol. 12, no. 8, p. 1691, 2020, doi: http://doi.org.10.3390/polym12081691

[22] D. Permana, E. Ilimu, N. M. Faariu, A. Setyawati, L. O. Kadidae, L.O.A.N. Ramadhan, “Synthesis and Characterization of Chitosan-Polyvinyl Alcohol-Fe2O3 Composite Membrane for DMFC Application,” *Makara J. Sci.*, vol. 24, no. 1, pp. 1–9, 2020, doi: http://doi.org.10.7454/mss.v24i1.11723

[23] J. Vera, E. Mosquera-Vargas, J. E. Diosa, “Thermal, electrical and structural study of polymeric membranes based on poly(vinyl alcohol), chitosan and phosphoric acid,” *Appl. Phys. A*, vol. 128, no. 5, p. 377, 2022, doi: http://doi.org.10.1007/s00339-022-05526-9