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Viscoelastic deformation of sulfonated polymeric cation-exchange membranes exposed to a pressure gradient

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HIGHLIGHTS

- Polymeric membranes area deformation exposed to a pressure gradient is investigated.
- The Zener model is applied to analyze the membrane deformation.
- The membrane area change depends on the time, showing a viscoelastic behavior.
- The greater the applied pressure gradient, the lower the membrane area change.
- The complete membrane area change depends on the membrane structure.

GRAPHICAL ABSTRACT
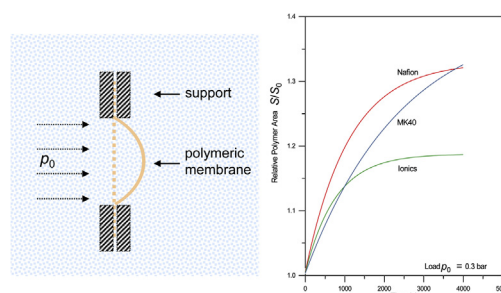
ARTICLE INFO

ABSTRACT

A permeation process is used as technique to study the viscoelastic properties of three commercial sulfonated polymeric cation-exchange membranes with different morphology. The Zener model was applied to interpret the deformation of the membrane area caused by the application of a hydrostatic pressure difference. The method permits to obtain information about the elastic and anelastic behaviors of the polymer thin film and the retardation time, and to estimate the membrane area change due to its deformation in a liquid medium. The results show that all the investigated membranes have a similar behavior, with a greatest area deformation at lower pressures mainly caused by the time-dependent anelastic strain, although differences are observed depending on the membrane structure.

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1. Introduction

Cation-exchange membranes find applications in many processes. For this reason membrane technology has obtained much attention in the industry and in research centers and there is an increasing necessity of versatile and economical separations processes to apply, for example, in biotechnology [1], wastewater treatment [2], fuel cells [3], etc. Most of the interesting materials for the construction of exchange membranes are polymers and it is frequent the use of conducting polymers as exchange membrane materials. For example, perfluorinated membranes, and among them Nafion membranes in hydrogen form, are currently used as solid polymeric electrolyte in fuel cells [3]. The viability and performance of cation-exchange membrane processes in practical applications is a function of membrane properties. Particularly, the mechanical properties of thin polymeric membranes are of wide interest to control processes because they affect the durability and lifetime.

Generally, fuel cell durability is highly correlated to viscoelastic properties of proton exchange membranes, which are time and

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temperature dependent physical properties, and many researchers have focused on the investigation of their viscoelastic properties. For this reason, the mechanical properties of Nafion membranes have been widely studied during the last decades, mainly using tensile stress–strain measurements and dynamical mechanical analysis [4].

Characterizing the viscoelastic properties of thin polymeric films is important and, in general, conventional mechanical testing methods are limited for such characterization due to the fragility of the films. Although recent advances in instrument development have been available for characterizing these properties, they are often complex and expensive and are difficult to perform for the creep test [5,6]. On the other hand, different studies show that the viscoelastic response of a polymeric membrane strongly depends on the environmental conditions of temperature and humidity due to the membrane hydration affects the mechanical properties [6–16]. In most of these works, the common testing conditions are "dry" samples or samples at different conditions of temperature and relative humidity, but also samples exposed to liquid water are studied [8,11,12]. However, other media different to the aqueous one could be interesting, for example in direct alcohol fuel cells, where the polymeric membrane is in an alcohol medium.

The Young's elastic moduli exhibits a marked decrease when hydration degree and temperature increase [7,8,17]. The main implication of reducing Young's modulus and yield strength is that it makes the polymeric membrane susceptible to permanent deformation, gradual weakening, and eventual failure when it is exposed to pressure gradients and pressure pulses. This fact is very important in pressure-driven membrane processes as reverse-osmosis, nanofiltration, ultrafiltration or microfiltration, which are already applied on an industrial scale to food and bioproduct processing [18].

In this work, we present a method which would allow the study of the mechanical behavior of a thin polymeric membrane immersed in any liquid medium by analyzing the time dependence of the pressure difference established at both side of the membrane during a simple permeation process. The method is based on the Zener model to describe the viscoelastic deformation of the membrane combined with experimental results. Results reported in other works have demonstrated that this model can be used in uniaxial tensile and stress-relaxation tests, and permit to estimate linear deformation, elastic moduli and viscosity [14,19]. The main novelty of the method is that it could be also used to estimate the area change of the polymeric membrane during the process and thus to estimate the true membrane area exposed to the flux, without the need for additional measures. This parameter is very important in those pressure-driven membrane processes which operate in dead-end mode. This mode is the one where the flow of water is perpendicular to the membrane surface. The water is pushed through the membrane by pressure and the stream of the feed flows vertically toward the membrane surface [18].

2. Basic equations

Linear Irreversible Process Theory [20] establishes linear relationships between the applied forces, X_k, and the fluxes, J_i, trough the membrane:

$$J_i = \sum_j L_{ij} X_j \tag{1}$$

where L_{ij} are the phenomenological coefficients. For a system consisting of a cation-exchange membrane separating two compartments containing only water and maintained at the same temperature but a different hydrostatic pressure, the transport equation for matter simply is:

$$J_V = L_p \Delta p \tag{2}$$

where J_V is the volume flux, Δp the pressure difference established between two sides of the membrane, and L_p is the so-called hydraulic permeability coefficient. Thus, the estimation of L_p can be made, in a typical permeation experiment, from the determination of the volume flux through the membrane under a constant applied hydrostatic pressure difference. In the linear regime, the hydraulic permeability coefficient can be obtained from the slope of the straight line obtained when the experimental volume fluxes are represented as a function of the applied pressure differences. Since the matter flux is proportional to the effective area of the membrane exposed to the flux, the coefficient uses to be expressed per unit membrane area.

When a uniform pressure gradient is established between both sides of a membrane, the relationship between the applied net force, F, and the pressure difference, p, it is given by:

$$F = (p_2 - p_1)S = pS \tag{3}$$

where S is the membrane area, and p_1 and p_2 are the pressures at both sides of the membrane. If the force is kept constant, at an initial value F_0, and the membrane area does not change, the pressure difference established between both sides of the membrane, p_0, will also be constant with a value equal to the initial value given by:

$$p_0 = \frac{F_0}{S_0} \tag{4}$$

where S_0 is the initial membrane area, in the absence of applying force. If the membrane area changes in the time, the pressure difference established between both sides of the membrane will change in spite of the applied load remains constant.

It is known that polymers have a viscoelastic nature which rises to time-dependent phenomena such as creep and stress relaxation [5]. The stress and strain induced when a load is applied are time functions. Creep in polymers can be quite significant, even at room temperature, and is rapidly accelerated by an increase in temperature or load.

According to the literature [5,7–14,17,20–24], when a viscoelastic material is subjected to a constant load, it deforms continuously. It has been shown by several authors that the viscoelastic deformation under constant load conditions, p_0, can be described satisfactorily using the Zener or standard linear solid model [14,19,21]. According to this model, the linear strain is a function of time t given by:

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{p_0}{E_a} + \frac{p_0}{E_m}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \tag{5}$$

where Δl and l_0 are, respectively, the length change and the initial length in the absence of load, E_a is the elastic modulus, related to the instantaneous elastic extension, E_m the anelastic modulus, related to the retarded extension, and τ is the so-called retardation time.

On the other hand, previous researches [25,26] reveal that the deformation of a thin membrane under a uniform pressure has revolution symmetry, i.e. the system does not change with a single rotation around a fixed axis. Even if this is an inhomogeneous deformation, the strain tensor could be averaged in the maximum curvature region and the relative change of area, $\Delta S/S_0$, could be considered in first approximation proportional to the relative change in the profile length, that is: