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Kinetic studies of the degradation of poly(vinyl alcohol)-based proton-conducting membranes at low temperatures

J.M. Morancho*, J.M. Salla, A. Cadenato, X. Fernández-Francos, X. Ramis, P. Colomer, Y. Calventus, R. Ruíz

Dept. Màquines i Motors Tèrmics, Universitat Politècnica Catalunya, Diagonal 647, 08028 Barcelona, Spain

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ABSTRACT

Thermal decomposition of unmodified poly(vinyl alcohol) (PVA) and poly(vinyl alcohol) crosslinked with sulfosuccinic acid (SSA) membranes has been studied using thermogravimetry (TGA) and ATR Fourier transform infrared spectroscopy (ATR-FTIR). Both types of membranes degrade in a two-step process. However, the introduction of SSA leads to an advance of the decomposition steps at very low temperatures. The reduction in the hydrogen-bond interactions of hydroxyl groups of unmodified PVA because of the presence of SSA crosslinks and the catalytic effect promoted by sulfonic acid group ($-SO_3H$) of SSA can contribute to this different behavior.

The kinetics of thermal degradation was investigated by TGA and derivative TGA (DTGA) curves from experiments under non-isothermal conditions at different heating rates. The Friedman isoconversional differential method was used to calculate the activation energy as a function of the reaction weight loss without any previous assumption on the kinetic model. For a representative stage of decomposition, pre-exponential factor and kinetic model were also obtained. Postcuring isothermal treatments and ATR-FTIR analysis of selected membranes have been used to verify the TGA analysis and add additional information.

1. Introduction

Poly(vinyl alcohol) (PVA) is a well-known low cost synthetic polymer, that is non-toxic, water-soluble, biocompatible and biodegradable with excellent mechanical properties. It possesses the capability to form hydrogels and membranes by chemical or physical methods. It has been widely used in a variety of fields such as the textile, cosmetics, paper industry, packaging and food production. It is also used in a variety of pharmaceutical and biomedical applications [1–3].

Proton-exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), employing hydrogen and liquid methanol as a fuel, have been explored as the technology of choice for clean and efficient energy-conversion systems for automobiles, portable applications, and stationary power generation. The proton-exchange membrane (PEM) is a central and critical component in PEMFCs and DMFCs. As a result, there is much interest in the study and development of such membranes. The membrane must possess a suitable combination of properties: high proton conductivity, good mechanical and chemical stability, low permeability, limited swelling in the presence of water and fabrication costs appropriate for the application [4,5].

The most commonly used and investigated membranes are of the perfluorinated type, of which Nafion® (DuPont) is the ubiquitous and best representative. In these membranes the ionic function is covalently attached to the polymer backbone, and is most often a sulfonic acid group ($-SO_3H$).

In DMFCs applications, Nafion® membranes present, in addition to their high cost, a high osmotic drag, which makes water management at high current densities difficult and a high methanol crossover (methanol, crossing over from the anode side through the membrane to the cathode side, reacts with oxygen, produces heat, and reduces the energy-conversion efficiency) [6,7].

In recent years, there has been an intensive effort and a significant progress in the development of low-cost materials suitable for DMFC membranes. Among them, poly(vinyl alcohol)-based proton-conducting membranes, due to their high selectivity for water with respect to alcohols and film-forming characteristics, have been suggested as a promising alternative. Sulfosuccinic acid (SSA) has been commonly used as a crosslinking agent to form an inter-crosslinked structure. Moreover SSA acts as sulfonating agent [8,9]. Scheme 1 shows the basic crosslinking reaction. The use of SSA, as a crosslinking agent, increases proton conductivity of PVA-based polymer electrolyte membranes and simultaneously reduces methanol permeability [10]. On the other hand, the crosslinking of PVA and the presence of protonic acid alter the chemical and thermal behavior of the PVA–SSA membranes and their stability with respect to unmodified PVA ones.

* Corresponding author. Tel.: +597 34 934016531; fax: +597 34 934017389.
E-mail address: morancho@mmt.upc.edu (J.M. Morancho).

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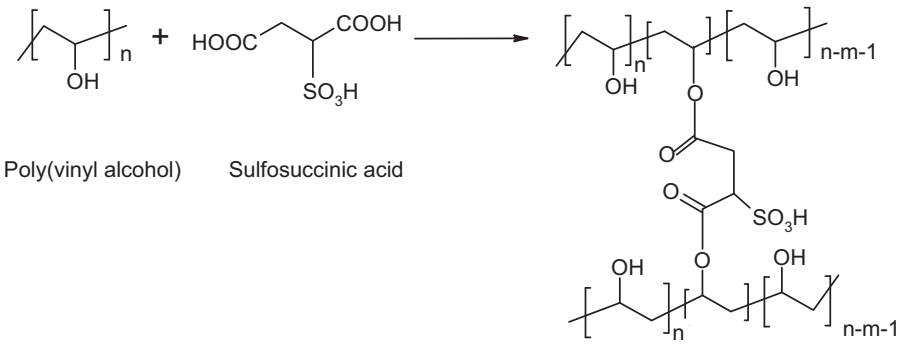


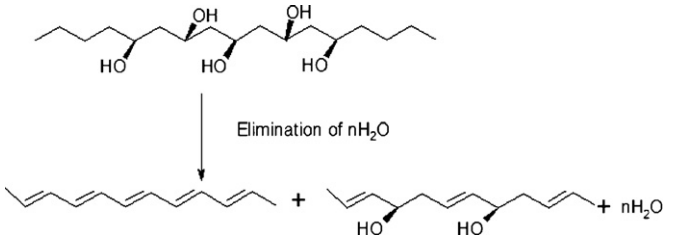
Scheme 1. PVA–SSA crosslinking reaction.

It is well known the relatively high sensitivity of PVA to thermal degradation at temperatures above and near its melting temperature and it has been the subject of several publications [11–15]. It is generally accepted that PVA thermally degrades in two steps. The first degradation step mainly involves the elimination reactions, while the second one is dominated by chain-scission and cyclization reactions [15,16]. The elimination reactions are mainly dehydration reactions that involve elimination of side groups from the main chain and the loss of water. As a consequence, a growing number of unsaturations appear in the main chain, which progressively turns into a polyene structure (see Scheme 2). When polyene structures are formed, the remaining OH pending groups act as weak links from where the non-conjugated polyenes can be snipped into low molecular structure via chain-scission reactions. The presence of acidic compounds can promote and accelerate these elimination reactions by protonating OH groups.

It is reported that the first degradation stage takes place from 130 °C to 260 °C. Above these temperatures, the degradation continues by chain scission and formation of compounds of low molecular weight.

Thermal stability studies of PVA and PVA–SSA membranes are a matter of great technical interest. In order to enhance their mechanical behavior, after their fabrication using a standard solution-cast method, usually a postcuring treatment at temperatures above 100 °C is performed. With the kinetic analysis of thermal degradation, a reliable evaluation of the kinetic parameters allows a theoretical interpretation of the experimental data and provides a mathematical description needed to extrapolate the stability behavior to different conditions from the experimental ones.

This work compares the thermal degradation of unmodified poly(vinyl alcohol) (PVA) and poly(vinyl alcohol) crosslinked with sulfosuccinic acid (SSA) membranes that have been studied using thermogravimetry (TGA) and ATR Fourier transform infrared spectroscopy (ATR-FTIR). It has seen that degradation of PVA–SSA membranes takes place in two steps, in a similar way to the unmodified PVA. However, the introduction of SSA crosslinker leads to remarkable changes in the degradation process. It causes an advance of decomposition steps at very low temperatures. Two facts can contribute to this different behavior: the reduction in the hydrogen-bond interactions of hydroxyl groups of unmodified PVA because of the presence of SSA crosslinks and the catalytic effect promoted by sulfonic acid group (–SO_3H) of SSA.



Scheme 2. Elimination reactions of H_2O.

The kinetics of thermal degradation of PVA and PVA with different SSA content was investigated by TGA and derivative TGA (DTGA) curves from experiments under non-isothermal conditions carried out in nitrogen atmosphere at heating rates of 2.5, 5, 10 and 15 °C min^{-1}. Although the papers found in the literature use first or nth order kinetic models, in this work, the thermal degradation kinetics has been interpreted in terms of multi-step degradation mechanisms. The widely used Friedman isoconversional differential method was used to calculate the activation energy as a function of the degradation weight loss without any previous assumption about the kinetic model or the activation energy [17,18]. For a representative stage of decomposition, beside activation energy, pre-exponential factor and kinetic model were also obtained. Postcuring isothermal treatments and ATR-FTIR analysis of selected membranes have been used to verify the TGA analysis and add additional information.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, 99% hydrolyzed, average Mw: 89,000–98,000 g mol^{-1}) and sulfosuccinic acid, as the basic crosslinking agent (SSA, 70 wt% solution in water), from Aldrich were used as received.

2.2. Preparation of the membranes

The membranes were prepared using a standard solution-cast method. PVA powders were dissolved in de-ionized water with continuous stirring at 90 °C to form a 10 wt% PVA aqueous solution until a transparent solution was obtained. A given amount of SSA of a desired concentration was then added to this PVA solution and the mixture was stirred continuously until a homogeneous solution was obtained. The proportions of SSA used vary from 0% to 25%. The membranes were cast by pouring the solution onto Petri dishes and evaporating water under ambient conditions for 16 h. When visually dry, the membranes were peeled from the plastic substrate, and had a thickness of about 0.1–0.3 mm. Some samples were performed with a post-treatment in an oven at different temperatures between 90 °C and 150 °C for 1 h.

2.3. Characterization and measurements

2.3.1. Degradation and stability analysis

The thermal stability of the membrane was evaluated using a thermogravimetric analyzer (Mettler TG50). The weight changes