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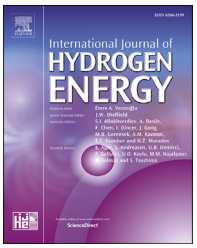

Gamma irradiation of polystyrene-co-acrylic acid copolymers to use them as membranes in fuel cells

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ABSTRACT

Styrene-co-acrylic acid copolymers were synthesized by radical bulk polymerization in a 96:4 M ratio and subsequently sulphonated with a mixture of sulphuric acid (170% of the molar amount of benzene rings theoretically present in the copolymer) and silver sulphate (0.11% of the sulphuric acid), the latter used as a sulphonation catalyst. Membranes were prepared from the sulphonated copolymers by "casting" their THF solution (0.2 g/mL). Membranes were exposed to γ radiation at several doses (10–100 kGy) in an industrial irradiator, at 10 kGy/h of dose rate. Membranes were spectrophotometrically characterized by FTIR, thermally by DSC and TGA and mechanically by TMA (including irradiated ones). DSC results show an increase in the glass transition temperature (Tg) of the copolymer, with respect to their homopolymers and further reduction with sulphonation time, which is related with a plastification effect of the water in the polymer; FTIR show the presence of the characteristic functional groups of the synthesized and sulphonated copolymers. TGA demonstrated a lower thermal stability along sulphonation time. Complex modulii, evaluated by TMA, is greatly enhanced along irradiation dose, however, a lightly reduction for sulphonated copolymers, corroborating the water effect for hydrophilic materials. Gel percentage results observed similar trends for irradiated sulphonated materials.

Introduction

There is a worldwide perception related to the reduced availability of non-renewable energy resources (oil and derivatives), and as a consequence, there is also an intensive trend for searching new methods for energy generation [1]. The difference is that such methods involve a reduction in environment pollution. Alternatives, from the technical point of view are the fuel cells [2]. They are electrochemical energy generators, using the energy involved into chemical reactions between a fuel and an oxidant. The main components of a fuel cell are the anode, cathode and the electrolyte [3].

There are various types of fuel cells, however the ones containing a polymeric electrolyte (PEMFC) are some of the most studied and advanced nowadays. The latter have as a key component the proton exchange membrane, which is in charge of transporting protons from the anode to the cathode.

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Membranes are evaluated by their polyelectrolyte yield, measuring characteristics as ion exchange conductivity (IEC), water absorption (WU) and proton conductivity [4,5].

However, it is also of similar importance for membranes to have useful mechanical properties, in order to have and maintain their properties against the several conditions to which they are exposed: catalyst incorporation, compression forces during assembly of MEA, pressure during PEMFC closing, dimensional changes during hydration and dehydration of the membrane, pressure from the fuel (liquid or gas), temperature, etc. [6].

Nafion membranes are up to now, the perfluorosulfonated ionomers most used as polyelectrolytes; although high fuel permeation (for DMFC), low humidity and low ion conductivity at higher temperatures, limit the performance of such materials. There are also Nafion systems based on polymer composites, where the inorganic material is in charge of holding water molecules through the −OH groups they regularly have into their structure. Such systems have improved proton conductivity and enhanced thermal and mechanical properties. However, when Nafion is in contact with water, its Young's modulus is reduced, since solvent has a direct impact in the tension-deformation relationship. Water or any other solvent swell the membrane, reduce their intermolecular forces and increase elongation; as a consequence, membrane is more ductile and susceptible to permanent deformation [7,8].

Ionizing radiation, usually accelerated electrons and gamma radiation, has been used intensively to produce structural crosslinking in polymers and in turn, enhance mechanical properties. Membranes has been optimized by such methods, Masson et al. [9] used a gamma radiation source to graft low density polyethylene (LDPE) with acrylic acid followed by sulphonation. Other authors [10] used 10 and 20 kGy of gamma radiation to enhance the degree of grafting on polyethylene based anion exchange membranes.

Considering the previous, control of mechanical properties is of vital importance for new materials pretending to be used as ion exchange membranes, but initial steps consist of preparing the polymeric material, which can be sulfonated without relevant changes in the base polymer structure. In this work, we have synthesized a polystyrene-co-acrylic acid copolymer, which was sulfonated and then treated with gamma radiation, expecting to have benefits on mechanical properties after crosslinking with such irradiation.

Materials y methods

Materials

Styrene (St, 99%, Aldrich) was purified with NaOH, dried with $CaCl_2$ and finally distilled under reduced pressure. Phenothiazine was added to acrylic acid (AA, 99%, Aldrich) and the monomer distilled under reduced pressure. Benzoyl peroxide was used as copolymerization initiator (BPO, Aldrich). Sulphuric acid (H_2SO_4, JTBaker), silver sulphate ≥99.0% (Aldrich) and anhydrous dichloromethane ≥99.8% (Aldrich) were used during the sulphonation procedure and Tetrahydrofuran ≥99.9% (THF, Aldrich) for membrane preparation.

Methods

Co-polymerization procedure

Synthesis was carried out trough a mass copolymerization reaction of styrene and acrylic acid in a 94/6 M ratio. Benzoyl peroxide was added as initiator (0.05% mol of total amount of comonomers). Reaction temperature was kept at 100 °C with a 250 rpm mechanical stirring under nitrogen atmosphere during 2 h. Copolymers were dried into a vacuum oven at 40 °C until constant weight.

Sulphonation procedure

Copolymers were sulphonated with sulphuric acid at a 170% mol (theoretical amount of benzene rings) and 0.055 5 mol of silver sulphate used as catalyst [11]. Each copolymer was dissolved in dichloromethane using 250 rpm mechanical stirring and 40 °C under nitrogen atmosphere. Sulphuric acid was mixed with silver sulphate and then added to the copolymer and reaction allowed to progress during 1, 2 or 3 h. Sulphonation reaction was terminated by removing the solvent and adding cold distilled water. Sulphonated copolymer was washed with abundant distilled water until reach pH ≈ 7 and then dried at ambient temperature with an air stream during 48 h.

Preparation of membranes

Films were prepared by casting, dissolving 0.2 g/ml THF and then poured into a glass container and left to dry into a fume cupboard until constant weight.

Irradiation of membranes

Membranes were inserted into a sample chamber and then placed in a well-known position into the compartment of an industrial gamma irradiator (JS-6500). The irradiator belongs to the Instituto Nacional de Investigaciones Nucleares (ININ). Time was calculated for the samples to obtain doses from 10 to 100 kGy for no sulphonated membranes, and 50, 75 and 100 kGy for sulphonated ones, to evaluate the effect of crosslinking among copolymer chains.

Characterization

Infrared spectroscopy (FTIR)

FTIR was used to evaluate presence of functional groups from the synthesized copolymers and compare with sulphonated ones; a ThermoNicolet Avatar 330 instrument was used under following conditions: 25 scans at the 4000–400 cm^{-1} region and a resolution of 4 cm^{-1}. Samples consisted of thin films from membranes and lecture taken through transmission.

Thermogravimetric analysis (TGA)

Thermal stability of sulphonated copolymers was evaluated by TGA. A thermobalance instrument from DuPont model 951 was used, with a heating rate of 10 °C/min from ambient temperature up to 700 °C under nitrogen atmosphere.

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