Vibrational spectroscopic study of pure and silica-doped sulfonated poly(ether ether ketone) membranes

Vijay Shankar Rangasamy [a,*], Savitha Thayumanasundaram [a], Jin Won Seo [b], Jean-Pierre Locquet [a]

[a] Department of Physics and Astronomy, KU Leuven, Bus 2414, Celestijnenlaan 200D, 3000 Leuven, Belgium
[b] Department of Metallurgy and Materials Engineering, Kasteelpark Arenberg 44 – Bus 2450, B-3001 Leuven, Belgium

HIGHLIGHTS

- FTIR peak area ratio correlated to crystallinity of SPEEK membranes.
- Linear relationship was observed between degree of sulfonation and crystallinity.
- Validating the technique for other polymers with carbonyl groups suggested.

GRAPHICAL ABSTRACT
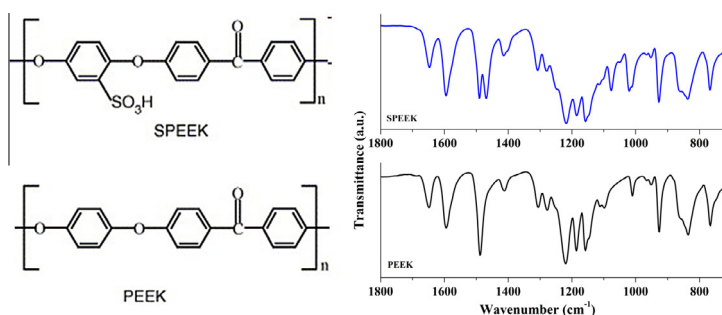
ABSTRACT

We report the vibrational properties of sulfonated poly(ether ether ketone) (SPEEK) membranes, used as electrolytes in proton exchange membrane (PEM) fuel cells, studied by Fourier transform infrared (FTIR) spectroscopy. We discuss the changes in the vibrational modes of the functional groups present in the polymer arising due to the sulfonation process and the subsequent incorporation of silica particles functionalized with sulfonic acid group. From the infrared spectra, we confirm the incorporation of sulfonic acid group in the polymer chain as well as in the functionalized silica particles. We have also measured the variations in the peak area ratio of the characteristic out-of-plane vibrations of the aromatic rings in the PEEK polymer at 1280 cm^{-1} with respect to a reference peak at 1305 cm^{-1}. These values were correlated to the crystallinity (X_C) values experimentally determined by DSC technique, providing a non-destructive means to calculate the crystallinity of polymer membranes. The calculated X_C values were in good agreement with the experimental values. The crystallinity was observed to decrease with increasing degree of sulfonation (DS), indicating the crystalline-to-amorphous phase modification of the polymer by sulfonation, which along with the enhanced ion-exchange capacity and water uptake, is responsible for the improved ionic conductivity at higher DS values.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Energy is arguably the most critical problem of this century, thanks to the growing demands of transportation, residential, and industrial consumption. In addition to meeting this demand, modern energy sources must be sustainable, environment-friendly, and immune to market fluctuations. Fuel cells are considered the ideal solution to meet these challenges and create a sustainable 'hydrogen economy' [1]. Among the various types of fuel cells, proton exchange membrane (PEM) fuel cells have reached grid parity with conventional power-generating technologies [2], in particular for transportation [3].

---

* Corresponding author.
  E-mail address: vijayshankar.rangasamy@fys.kuleuven.be (V.S. Rangasamy).

In a PEM fuel cell, the proton exchange membrane is the performance-limiting component which plays a dual role—as an ionic conductor between the anode and the cathode—and as an electronic insulator between the electrodes to facilitate electron flow through an external electrical circuit [4]. Hence, the study of membrane properties is indispensable for the understanding and improving the performance of a fuel cell. Nafion® has been the standard electrolytic membrane used in most commercial PEM fuel cells so far, albeit with problems such as thermal degradation above 120 °C and high methanol crossover when methanol is used as the hydrogen source [5]. Poly(ether ether ketone) (PEEK), a semi-crystalline aromatic thermoplastic polymer, has been one of the widely studied alternative polymers owing to its robust thermal and mechanical properties and exceptionally low methanol crossover [6–8]. PEEK is used in several demanding industrial applications such as ultra-high vacuum device components, as a biomaterial in medical applications [9,10], and in aerospace [11,12] and automotive industries [13]. In its sulfonated form, PEEK is one of the most promising ionomers in terms of cost and performance at high temperatures. Sulfonated PEEK, or SPEEK, combines the thermo-mechanical stability of the semi-crystalline PEEK polymer and the ionic conductivity facilitated by the addition of sulfonic acid groups to the polymer chain.

Infrared (IR) spectroscopy is a powerful tool for qualitative analysis of compounds, especially for the identification of functional groups [14]. IR spectroscopy also serves as a valuable non-destructive tool to measure the crystallinity of polymers, as the IR spectrum is altered by structural changes in the crystalline regions of the polymer. These changes result in bond deformations and characteristic absorption peaks in the infrared spectra corresponding to the crystalline regions. To determine the degree of crystallinity (X_C) quantitatively, the absorption peaks that are sensitive to the crystallinity must be analyzed with respect to a reference peak. In the case of proton exchange membranes such as SPEEK, the thermo-mechanical and electrochemical properties—the proton conductivity in particular—are strongly affected by crystallinity. Therefore, the study of the crystalline state in such polymers is of immense importance. Although several reports on the characterization of sulfonated PEEK by FTIR spectroscopy are already available, these reports are often limited to functional group identification to prove the successful incorporation of the sulfonic acid (−SO₃H) group. There is not much information available on the dependence of the FTIR spectra on the degree of crystallinity of this polymer. Such a correlation gains importance as other non-destructive methods are not as sensitive as FTIR spectroscopy to the conformation and packing of molecular chains [15]. For example, the X-ray diffraction technique when applied to study polymer crystallinity is prone to the strong amorphous background that overlaps the small diffraction peaks arising due to the presence of some long-range symmetry in the polymer matrix.

In this study, we investigate the vibrational properties of SPEEK membranes by FTIR spectroscopy in attenuated total reflectance (ATR) geometry. The changes in the vibrational modes of the functional groups present in the polymer due to sulfonation and subsequent addition of sulfonated silica particles are studied. We also use this technique to calculate the degree of crystallinity of the

PEEK polymer by comparing the intensity of a crystallinity-sensitive peak with that of a reference peak. The areal ratio of these peaks is then correlated to the degree of crystallinity by comparing the results with the values experimentally calculated by Differential Scanning Calorimetry (DSC) technique. Such a non-destructive testing protocol could possibly aid faster quality control sequence at industrial level, thereby significantly bringing down the processing cost and time.

Materials and methods

Poly(ether ether ketone) (PEEK grade 450PF) was purchased from Victrex® and was sulfonated following the procedure reported earlier [16]. Typically, 5 g of PEEK powder was dried in a vacuum oven at 80 °C prior to sulfonation. The dried powder was then added to 95 mL of concentrated sulfuric acid (H_2SO_4, 95–98%, ACS), and continuously stirred in nitrogen atmosphere. SPEEK samples with three different degrees of sulfonation (DS) were prepared by varying the sulfonation temperature from room temperature to 60 °C and the reaction time from 5 h to 72 h. The initial concentration ratio of PEEK/H_2SO_4 was maintained at 5/95 (w/v) in all the experiments. The sulfonated polymer was slowly precipitated in ice-cold ultrapure water (18.2 MΩ). The collected SPEEK strands were washed thoroughly with ultrapure water until neutrality and then dried at 80 °C for 12 h in a vacuum oven for the removal of moisture. The chemical structure and the ¹H NMR nomenclature of the aromatic hydrogens in the SPEEK repeat unit are shown in Fig. 1. The DS values of the samples were determined by ¹H NMR spectroscopy from the ratio of the peak area of the distinct H_{13} signal to the integrated peak area of the signals corresponding to all the other hydrogens [17]. ¹H NMR experiments in solution-state were carried out on a Bruker Avance BBO 300 spectrometer at a ¹H Larmor frequency of 300.13 MHz at room temperature. A 3 wt.% solution of the polymer sample in deuterated dimethyl sulfoxide (DMSO-D6) was prepared for each analysis. The chemical shift of tetramethylsilane (TMS) was used as the internal standard reference.

Fumed silica obtained from Sigma–Aldrich was functionalized with sulfonic acid and used to prepare SPEEK-Silica composite membranes. 3-Mercaptopropyl tetramethylsilane (MPTMS) was used as the organosilane precursor to prepare the functionalized silica by a co-condensation method [18]. MPTMS was added dropwise to 2 g of fumed silica so that all the liquid was adsorbed by the silica. After a reaction time of 24 h at room temperature, the modified silica was oxidized with 32 mL of a 33% H_2O_2 solution and the suspension was stirred for 1 h at 60 °C. The solid phase was extracted from the mixture by centrifugation at 2500 rpm for 10 min, and then washed with ultrapure water. The extracted solid was then suspended in a 10 wt.% H_2SO_4 solution for 1 h and washed as before. Silica functionalized with sulfonic acid was obtained as the final product after drying the precipitate at 60 °C for 24 h in a vacuum oven.

To prepare sulfonated PEEK membranes, the SPEEK sample was dispersed in N,N-dimethylacetamide (DMAc) at room temperature to make a 10 wt.% solution. After the complete dissolution of SPEEK, the calculated amount (in weight percentage) of functionalized
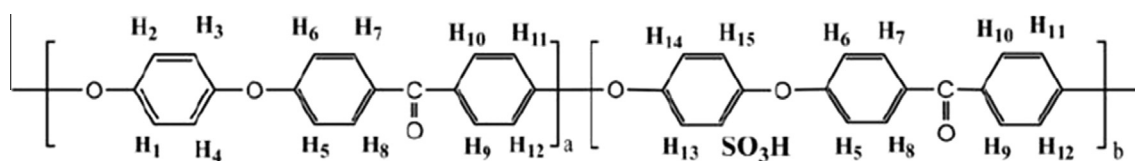

Fig. 1. Chemical structure and ¹H NMR nomenclature of protons in the SPEEK repeat unit.