Evaluation of radiation stability of electron beam irradiated Nafion® and sulfonated poly(ether ether ketone) membranes

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ABSTRACT

Proton exchange membranes (PEM), which have been commonly used in fuel cells have raised interest for the application in harsh environments involving ionizing radiation. Therefore, radiation stability and ability to sustain their functionality under the radiation environment are of great interest. Within this study, electron beam irradiation in dose range from 50 to 500kGy was used to evaluate the effects of radiation on the physico-chemical and mechanical properties of two types of PEM: commercial Nafion®117 and sulfonated poly(ether-ether-ketone) (SPEEK) with high degree of sulfonation (DS = 0.75±0.5).

SPEEK membrane presented higher mechanical and thermal stability compared to that of Nafion® at doses up to 250 kGy, which was evidenced by infrared and electron paramagnetic resonance spectroscopy, thermal analysis, ion chromatography methods. Tensile tests at room temperature and dynamical mechanical analysis of irradiated membranes revealed improved strength, storage modulus at room and elevated temperatures (80°C) for irradiated SPEEK as compared to pristine PEM. For comparison Nafion® exhibited notable deterioration of mechanical properties including elongation at break due to the predominant oxidation and chain scission already at doses exceeding 50 kGy. The study indicated that SPEEK could be perspective replacement of traditional PEM for application in fuel cells exposed to ionising radiation.

1. Introduction

Nafion®, the sulfonated tetrafluoroethylene-based fluoropolymer–copolymer, first synthesised by the DuPoint[TM] is a standard membrane material used for polymer electrolyte membrane (PEM) applications in fuel cells (FC), electrolysis cells, batteries and other electrochemical devices [1]. The polymer consists of hydrophilic perfluoro sulfonic acid moieties attached to a hydrophobic fluorocarbon backbone (Fig. 1a) and possess high conductivity not only for hydrogen protons, but also for various kinds of cations due to the presence of negatively charged sulfonate groups [2]. However, broader application of Nafion® have

several drawbacks such as high price, limited selectivity, permitted leakage between anode and cathode electrolyte compartments. All of this leads to the enhanced search of alternative PEM materials. In recent decades, SPEEK polymers, the sulfonated polyether-ether ketone membranes (Fig. 1b) have been evaluated as alternative replacement to conventional PEM materials due to relatively lower costs and advanced properties including adjustable thermal and mechanical performance depending on the degree of sulfonation (DS) of the crystalline PEEK polymer under the effect of sulfonic acid under controlled reaction conditions, whereas the proton conductivity may be slightly lower or comparable with that of commercial PEM Nafion [3–6].

PEM based technologies are being considered for the use in industries related to harsh environments such as nuclear facilities, where fuel and electrolysis cells have found an application

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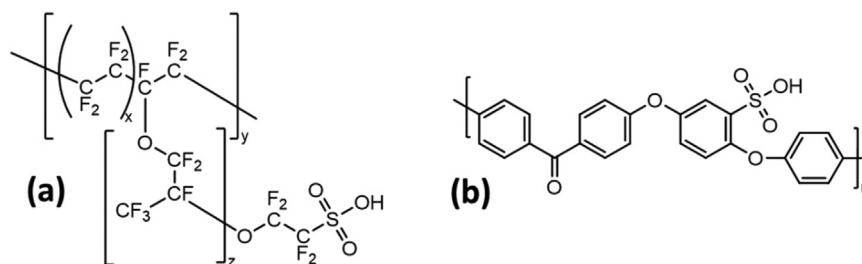 *E-mail address:* elina.pajuste@lu.lv (E. Pajuste).

Fig. 1. The general chemical structures of Nafion® (a) and SPEEK (b) polymers.

for separating and recovering heavy and radioactive hydrogen isotopes [7,8]. Electrolytic processing of water in order to decontaminate it from radioactive isotope of hydrogen, tritium, is an example of PEM being exposed to ionizing radiation [9,10]. Tritium is a beta (β-) radiation emitter of a half-life of 12.3 years and is a by-product in fission and a main fuel in nuclear fusion reactors. Therefore, radiation stability and ability to sustain functionality under the radiation environment of the membrane material is of great importance.

Radiation stability studies of Nafion® membrane have demonstrated considerable reduction of mechanical and thermal stability due to the degradation of polymer backbone within free radical induced reactions. Radiation stability has been assessed after irradiation with either gamma of electron beam radiation in dose ranges up to 500kGy [11–15]. Moreover, a dedicated study of tritium beta radiation effects has been performed by Hongqiand et al. by immersing the membranes in the tritiated water ($\sim$12TBq/L). Results of other author studies indicated to increased fluorine anion concentration released in the water containing Nafion® after exposure to 200kGy as a result of radical induced -CF_2 backbone degradation and release of fluorine anions and atoms as the primary products of radiolysis [16]. In addition, direct ionizing particle interaction with the polymer molecules radiation chemistry of the surrounding environment should be considered. In water environment water radiolysis products, such as H, OH radicals, H_2O_2, may have significant role in the radiolysis reactions as reported by Ghassemzadeh et al. [17]. Moreover, water radiolysis has an effect also due its high content in the polymer itself and in this case the products are formed within the polymer that leads to the destruction throughout all the volume of the material [11]. It must be emphasized that destruction products of the fluorine containing polymer are toxic, corrosive and possess danger both to the employees and environment [18]. For example Balko and Chaklos reported of several volatile products such as CF_4, COF_2, CF_2=CF-CF_3 formed during degradation of Nafion® [11].

It can be expected that SPEEK possess higher radiation stability due to the aromatic polyether-ether ketone backbone. It is well known from the radiation chemistry of organic compounds that aromatic polymers are radiation resistant since π-electrons of the aromatic system are shared by the entire system and an excitation of π-electron does not represent a concentration of energy at a particular location in the molecule. Additionally, the aromatic system due to the resonance phenomena can also act as an energy sink for energy absorbed by other parts of the molecule, affecting increased thermal stability and stability under influence of exposure to non-ionising (UV) and high energy ionising radiation [19].

To assess mechanisms of radiation effects a low temperature (77K) irradiation has been performed by Li et al. and formation of radicals was observed during these studies by the electron spin resonance (ESR) measurements. However, after storage for less than 20 minutes or thermal annealing the ESR signal was diminished due to the rapid radical decay [20]. The mechanisms of the radiation effects of PEEK are considered to be simultaneous crosslinking and scission under the high dose irradiation of electron beam, whereas under gamma irradiation in air chain scission occurs mainly on the surface, whereas crosslinking within the bulk of the polymer [21]. As mentioned above, the irradiation environment is of great importance, therefore. There have been reported comparative studies of PEEK and other polymer radiation resistance under oxidative conditions, where PEEK demonstrated its superior properties regarding the exposure to harsh environments [21]. It must be emphasized that PEEK has been considered and already has been used as a base material for radiation shielding composite materials [22]. It has been approved for the application in spacecrafts and nuclear fusion reactors, where the exposure to radiation can reach 50MGy or greater doses [23]. Therefore, a high dose exposure studies have been implemented up to 100MGy [24]. The main interest of the high dose studies included assessment of the change of the thermal properties [25]. Aging studies of PEEK with simultaneous exposure to high temperature and gamma irradiation has shown that degradation is mainly induced by heat. Study performed by Yang et al. demonstrates that thermal degradation mechanism of PEEK is based on scission of the aromatic ether bonds generating radicals followed by the oxidation and crosslinking [26].

All of the studies described above regarding the radiation stability were performed for PEEK, however, there is a lack information on the sulfonated polymer available.

Moreover, there is an interest of direct comparison of Nafion® and SPEEK performance in radiation environments. Currently, there is a data of comparably low dose Nafion® radiation resistance and high doses for PEEK.

The aim of the study was to evaluate the effect of ionizing radiation on the mechanical, thermal properties and proton conductivity of Nafion® and sulfonated poly (ether ether ketone) (SPEEK) proton exchange membranes (PEM) under identical irradiation conditions. The irradiation dose range was chosen regarding the potential exposure conditions in future applications. In ITER, the International Thermonuclear Experimental Reactor, an electrolyser should maintain its performance during 2 years of operation in tritiated water of 9 TBq/kg which corresponds to the irradiation of about 530 kGy [27].

2. Materials and methods

2.1. Materials

Commercially available Nafion® 212 and Nafion® 117 membranes of 50.8 μm and 183 μm thickness both were purchased from Chemours Company (Wilmington, Delaware, USA). Before their use, the polyester cover sheets and backing films were removed. Poly(ether ether ketone) (PEEK) granules were obtained from Sigma Aldrich (MO, USA). Other materials and chemicals used for the sulfonation of PEEK, development, and testing of membrane materials (sulfuric acid, N,N-dimethylformamide, etc.) were of reagent grade and used as received. Sulphate anion (SO_4^{-2})

standard (1000 mg/L) for ion chromatography (IC) was purchased from Hach Lange GmbH (Dusseldorf, Germany). Fluoride (F^-) standard (1000 mg/L) for IC was purchased from Sigma Aldrich (USA). Ultrapure deionised water was generated by a Millipore Milli-Q^{TM} system (Billerica, MA, USA).

2.2. Preparation of SPEEK membranes

PEEK pellets were dried in a vacuum oven at 100°C overnight. Then appropriate weight (10 g) of the PEEK was dissolved in 200 mL of concentrated sulfuric acid (98%) and vigorously stirred at room temperature for 24 h. Afterwards obtained polymer solution was placed in a thermostat and heated at 36°C for 24 h. The polymer suspension was slowly poured into a large amount of cool deionized water. The precipitated SPEEK polymer yarns were filtered, washed with deionized water until neutral pH and dried at 80°C for 24 hours. The procedure was repeated to obtain the necessary samples for membrane replicates.

SPEEK membranes were obtained by solvent cast method as follows: 0.5 g of the SPEEK polymer were dissolved in 20 mL of dimethylformamide followed by stirring at 100°C for 1 h. Then polymer solution was cast into Petri dish and dried for 24 h at 80°C to remove the solvent. The thickness of the prepared SPEEK membranes was 120±20 µm.

2.3. Irradiation

Irradiation was carried out by the Varian Clinac® medical accelerator at the Accelerator Laboratory of Jyväskylä University (Finland). Both Nafion® and SPEEK polymer films (3 replicates of each) were sealed in separate sterile polyethylene sample bags and irradiated in air at 0 (control), 50, 100, 250, and 500 kGy of 6 MeV accelerated electron beam (EB). In addition, membrane samples of 10 mg weight were immersed in deionised water and also irradiated at doses of 25 to500 kGy. The dose rate was equal to 1 kGy/min.

2.4. Methods of analysis

2.4.1. Degree of SPEEK sulfonation (DS)

Degree of sulfonation (DS) was determined by acid-base titration as described in literature [28]. 0.5 g of the dried SPEEK precipitate was properly weighted in a 100 mL conical flask and soaked in 25 mL of 0.1 M NaCl solution to provide exchange of H^+ to Na^+ of all sulfonated groups of SPEEK. Then samples were titrated with standardized 0.1 M NaOH solutions. The DS was calculated using the dry weight of the sample and the quantity of exchanged protons. The triplicate measurements indicated DS to be 0.75±0.05.

2.4.2. Fourier-transform infrared (FTIR) spectroscopy and FTIR-TGA

Bruker Vertex 70v vacuum spectrometer equipped with an attenuated total reflection (ATR) accessory was used in this study. Recording range 400 cm^{-1} - 4000 cm^{-1}, spectral resolution ± 2 cm^{-1}, in 2.95 hPa vacuum, at least 3 measurements par sample, 20 spectra per measurement, giving a sum of at least 60 spectra per sample were obtained. Average spectrum was calculated from the measured three replicate spectra. Data were collected using TRIOS Software v4.3.1 and FTIR program OPUS by Bruker, analysed within OriginPro v8.0 scientific graphing and data analysis software.

2.4.3. Ion chromatography

Ion chromatography (IC) was used to determine concentrations of dissolved fluoride and sulphate anions as the degradation products of irradiated membranes in water samples. Analysis was performed on a Dionex^{TM} Integrion^{TM} high pressure IC system from Thermo Fisher (MS, USA) equipped with Dionex ionPac^{TM} AS18-4µm (4×150 mmm) analytical column, Dionex EGC III KOH potassium hydroxide Eluent Generator and Dionex AS-AP autosampler. A

laboratory validated method for seven anion (fluoride, chloride, nitrate, nitrite, sulphate and phosphate) analysis was used. All chromatographic experiments were carried out in the isocratic mode, at 30°C. The operating conditions were: 1 mL/min eluent flow rate, 250 µL loop volume, 25µL sample injection volume, 124 mA current in suppressor. Water samples of 50 µL volume were diluted 1:10 in chromatographic vials with deionised water. Three replicates were tested for each of the samples including the control samples of non-irradiated deionised water. Seven-point calibration curves were obtained in the 0.05–0.5 mg/L concentration range for fluoride anions, and 0.05-5 mg/L for sulphate anions with the correlation coefficients $R^2 > 0.999$ to determine anion concentrations in the irradiated water samples. The method uncertainty (U, %) of 11% for F^- and 10% for SO_4^{-2} were used to evaluate the total RSDs (%). The levels of the quantification (LOQ) of the method were 0.05 mg/L for F^- and 0.5 mg/L for SO_4^{-2}, respectively.

The sample weights were used to calculate the concentration of anions formed from the degradation of PEM membranes [13].

2.4.4. Thermogravimetry analysis (TGA)

TGA measurements were performed using an Exstar SII TG/DTA 6300 (Seiko Instruments Inc., Chiba, Japan) thermogravimetric instrument. Samples of Nafion® and SPEEK membranes (~2.5 mg weight) were placed in alumina crucibles and tested under air flux (100 ml/min) from 25 to 950°C with a heating rate of 10°C/min. Three replicates were tested for each sample. The average TGA curves of the weight loss versus temperature and the derivative (DTG, %/°C) were analysed. For comparative reasons, the TGA data of the sulfonate group decomposition were used to calculate DS for SPEEK membranes after their EB irradiation. The Eq. (1) described in the literature [29] was used:

$$DS = n(SO_3H)/n(PEEK) = M(PEEK)/[(m/\Delta m) \times M(SO_3H)] \quad (1)$$

where M(PEEK) and M(SO_3H) are the molecular masses of PEEK monomer (288.7 g/mol) and =sulfonic acid groups (81 g/mol), m is the mass of SPEEK at the starting of the desulfonation, and Δm is the mass loss due to the desulfonation.

2.4.5. Differential scanning calorimetry (DSC)

Measurements of the calorimetric properties were provided on DSC 1/200 W equipment (Mettler-Toledo, Greifensee, Switzerland) equipped with intercooler. The preconditioned membranes samples at 55°C under vacuum for 48 hours were used for DSC analysis. Then samples with approximate weight of ~10 mg were placed in aluminium pans and tested under a constant nitrogen purge (60 mL/min). Samples were heated from −5 to 250°C at a heating rate of 1 0°C/min, conditioned at 250°C for 5 minutes, followed by cooling from 250 to −5°C at a cooling rate of 10°C/min. Samples were stored at this temperature for 5 min and further heated to 250°C at a heating rate of 10°C/min. The data from the subsequent heating–cooling–heating cycles were analysed by triplicate. Calibration of the instrument was performed with indium sample (T_m = 156.6°C). Pristine and electron beam irradiated Nafion® and SPEEK membrane samples were dried under vacuum until reaching constant mass and kept in the desiccator until analysis to reduce the impact of the adsorbed water on the calorimetric characteristics.

2.4.6. Mechanical properties

Mechanical properties were determined by constructing stress-strain curves at room temperature (23 ± 2°C) and relative humidity RH = 30 ± 2% using a Tinius Olsen H1KS universal tensile testing machine (PA, USA) equipped with 1kN strain gage load cell. Samples were cut as rectangles with a length of 70 mm (the gauge length of 50 mm) and a width of 5 mm. Crosshead moving
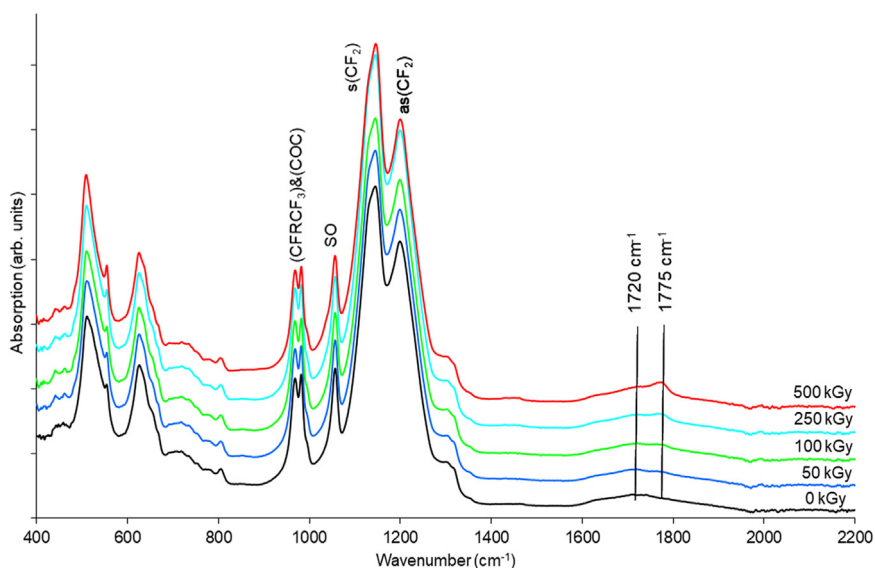
Fig. 2. FTIR spectra of pristine and electron irradiated Nafion® membranes.

speed was set to 10 mm/min during the tests. From the stress–strain curves, the modulus of elasticity, the tensile strength as the maximum stress at rupture and the elongation at break (were determined as well as the stress at yield was estimated in the case of semi-crystalline SPEEK membranes as the point of the intersection of the tangent lines to the regions corresponding to the elastic and plastic deformation. Dynamic mechanical analysis (DMA) was used for characterisation of viscoelastic properties, thermal transition stages, including the storage modulus under the glass transition, including at room temperature and conventional operation temperatures of PEM in the case of FC applications (80°C) that are lower to potential applications under hydrogen isotope exchange transition energies. For each type of membrane at least 5 parallel samples were tested, and the averaged values were compared. The experimental errors were estimated according to the Student's t-distribution.

2.4.7. Dynamic mechanical analysis (DMA)

Samples were preconditioned in vacuum oven at 55°C for 48 h prior to analysis to remove the absorbed water during the storage. DMA testing was performed at 1 Hz from -10°C to +250°C under nitrogen atmosphere on a DMA/SDTA861 instrument (Mettler Toledo, Columbus, OH, USA) in extension mode according to EN ISO 6721–2. Samples were cut in the pieces of 15 mm × 7 mm size and their dynamic mechanical thermal properties such as the dynamic storage modulus, loss modulus, and the damping factor (tan δ) were determined at the heating rate of 5.0°C/min.

2.4.8. Electron paramagnetic resonance (EPR) spectroscopy

EPR spectra were measured with Bruker ELEXSYS-II E500 CW-EPR spectrometer at room temperature. Magnetic field modulation parameters were 100 kHz and 0.1 mT; microwaves were generated at 9.834 GHz frequency and 20 mW power. Membranes were cut into smaller pieces (3×4 mm) and placed into EPR sample tubes. To estimate uncertainties, 5 different sample pieces were measured for each irradiation dose. EPR signal intensities have been calibrated to sample mass. EPR spectra simulations were performed in EasySpin software [30].

2.4.9. Proton conductivity

Conductivity measurements of non-irradiated and electron beam irradiated SPEEK and Nafion® membranes were performed through-plane using impedance analysis with various cell configurations as described in the previous study [31]. The conductivity was determined by means of impedance measurements using a BioLogic VMP3 multichannel potentiostat / galvanostat frequency response analyser (FRA) at AC amplitude of 10 mV with EC-Lab® software. The frequency interval employed for the measurements ranged from 10kHz to 10mHz. For the ionic conductivity, the membranes were immersed in a de-ionized water for 24 hours and kept in a chamber with a water bath. Samples were sandwiched between two copper discs with a diameter 10 mm. The pressure is kept constant and defined by the maximum limits of screws used to close the probe arrangement. Dry film thickness values were measured with a micrometre. Proton conductivity of the samples was calculated using the following Eq. (2):

$$\sigma = L/R * A, \tag{2}$$

where σ is the proton conductivity (S cm^{-1}), L the thickness(cm) of the polymer film, A the contact area between the electrodes and the polymer film, and R the bulk membrane resistance calculated from the Nyquist plot.

3. Results and discussion

3.1. FTIR spectra analysis

Fig. 2 shows typical spectra of non-irradiated and irradiated Nafion® membranes. All the spectra exhibited strong absorption bands at 1144 cm^{-1} and 1199 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of the branched -CF$_2$ groups, a narrow band at 1014 cm^{-1} associated with symmetric stretching S – O vibration of the – SO$_3{}^{2-}$ group, and two strong absorption bands allocated at 980 cm^{-1} and 960 cm^{-1} due to C –F and C – O – C stretching vibrations [32]. Some weak peak bands presented at 805 cm^{-1}, 630 cm^{-1}, 511 cm^{-1} and 550 cm^{-1} were associated with C – S and C – F stretching and bending vibrations [33].

Spectra of electron beam irradiated samples showed a formation of new weak broad signal around 1720 cm^{-1}, which could be associated with the presence of carbonyl groups or possible presence of low levels of hydrated protons or protonated water molecules in the form of hydronium ions [34]. Irradiation introduced broad weak band with a maximum around 1775 cm^{-1} that can be attributed to defluorination and formation of CF = CF bonds

Table 1

Anion contents in water extracts of irradiated Nafion® and SPEEK samples.

Dose (kGy)	Nafion®				SPEEK	
	SO_4^{2-} (mg/g$_{Polym.}$)	±RSD	F$^-$ (mg/g$_{Polym.}$)	±RSD	SO_4^{2-} (mg/g$_{Polym.}$)	±RSD
0	<0.005	-	<0.001	-	<0.005	-
50	0.07	0.01	0.15	0.02	<0.005	-
100	0.10	0.01	0.21	0.02	<0.005	-
250	0.39	0.04	0.76	0.08	0.14	0.01
500	1.15	0.12	1.49	0.16	0.26	0.03

and also the radiation induced scission at the vinyl ether groups and formation of C $=$ O bonds as a result of chain destruction and radiation induced oxidation during irradiation in air conditions [13,35]. Signal intensity at 1775 cm-1 correlates with the dose indicating the decomposition of polymer and formation of oxidation products [34]. Slight increase of the bond intensities at 511 cm^{-1} and 550 cm^{-1} has also been observed indicating the radiation induced decomposition of polymer (CF$_2$)n backbone.

FTIR spectra of pristine SPEEK contained several absorption bands, which are characterised in Fig. 3. The most intensive signal bands observed in SPEEK spectra were attributed to O – H and S $=$ O bond vibrations of the sulfonic acid at 1155 - 1217 cm^{-1}, stretching vibrations of C $=$ O at 1645 cm^{-1} and 1610 cm^{-1} attributed to acid and ketone groups, signals at 1480 cm^{-1}, 1217 cm^{-1} for benzene -Ph- groups and Ph – CO – Ph groups. and Number of signals (1020, 1080, and 1250 cm^{-1} some of most intense) can be attributed to for O $=$ S $=$ O band stretching and bending vibrations [36,37]. Broad peak at around 2820 cm^{-1} could be assigned to C - H stretching [38], and at 2950 cm^{-1} to C – H asymmetric stretch [39], whereas broad signal centred at around 3075 cm^{-1} could be assigned as – CH stretching [40]. Signals at 709cm^{-1} [41], 1308cm^{-1} [42], 1410cm^{-1} [43]corresponds to benzoyl ring, C $=$ O band and COO, respectively.

Electron beam irradiation at doses below 500 kGy did not cause notable changes to most of these absorption bands, whereas at 500 kGy increase of band intensities at 1280 cm^{-1}, 679-685 cm^{-1} and 790-840 cm^{-1}, as well as crystalline phase signals at 586 cm^{-1} was observed (Fig. 4).

Changes of the crystalline phase signal at 586 cm^{-1} could be attributed to the effect of high dose irradiation on reorganization of the chemical bonds and crosslinking, whereas the increase of O $=$ S $=$ O group signals at 1280 cm^{-1} associated with the formation of crosslinks between the molecules.

In most cases, when crosslinking of SPEEK was reported at doses up to 400 kGy, the ionising radiation treatment induced activation of crosslinking promoters containing active double bond (di- or tri-vinyl or acryl) additives, which acted as the secondary crosslinking agents affecting formation of crosslinking bounds between SPEEK molecules [37,44]. In this case, the absence of crosslinking agent and rather low irradiation time at doses below 250 kGy resulted in no changes in the structure comparing to irradiation up to 500 kGy.

3.2. Ion chromatography

Nafion® and SPEEK membranes were also irradiated in water and post irradiation measurement of the concentration of sulphate SO_4^{2-} and fluorine F$^-$ ions were done by the means or ion chromatography. Results are summarized in Table 1 and demonstrated in Figs. 5 and 6.

Water radiolysis products might play a significant role regarding the radiation resistance of the membrane materials. Radical reactions during irradiation of Nafion® have been described by Ghassemzadeh et al. [17] and simultaneous effect of water and temper-

ature by Yamaguchi et al. [45]. Ion emission indicates the degradation of the polymer. In case of Nafion® the fluoride ions are being released because of scission of the polymer chains. Results demonstrated strong correlation between the irradiation dose and fluorine ion concentration from 0.15 mg/g$_{Polym}$ after irradiation with 50kGy up to 1.49 mg/g$_{Polym}$ after - 500kGy. To compare both polymers the concentration of sulphate ions was also measured. An increase of sulphate ions was observed already at irradiation dose 50kGy for Nafion®, whereas for SPEEK slight release of sulphate ions was observed only at doses reaching 250 and 500kGy. Stability of macromolecular structures of Nafion® and SPEEK can be differently affected as further discussed in TGA results, which indicated lower stability of polytetrafluoroethylene backbone as compared to that of aromatic poly(ether- ether-ketone) backbone of SPEEK. The IC data were in good agreement with the results of FTIR analysis indicating increase of the degradation products in Nafion® correlating with the radiation dose above 100 kGy.

3.3. TGA analysis

Thermal stability is an important factor considering the PEMs, which are typically operated at temperatures around 80°C. When operating in harsh conditions, temperatures may also expand 100°C leading to potential thermal oxidation combined with ionising radiation effects resulting in reduction of the material performance of proton conductivity and decrease of operation lifetime. Figs. 7 and 8 show thermal decomposition behaviour of pristine and electron beam irradiated Nafion® and SPEEK membranes heated up to 950°C in air atmosphere.

TGA analysis of both SPEEK and Nafion® indicated that mass decrease was accompanied with exothermic signals due to exothermic oxidation of polymers.

Nafion® 117 membranes underwent three main thermal transitions. The initial stage at temperatures above 100°C was due to the desorption of water bounded to the sulfonic groups of Nafion® with the average weight loss reaching 4% at doses below 250 kGy (Fig. 7a). The calculated weigh loss was 7% at 500 kGy due to the radiation induced oxidation and formation of adsorbed hydrolysis products [46]. The second weight loss undergo at temperatures between 280 and 380°C and was associated with the degradation of sulfonic groups, decomposition of side chains – OCF$_2$CF$_2$ – SO$_3$H [47]. The third, multistep stage with several peaks determined by DTG ranged between 380 and 550°C (Fig. 7b) attributed to multistep radical reactions during the degradation of the polymer backbone chains CF$_2$ – CF$_2$ [48]. From the DTG curves it can be well seen that ionising radiation facilitates the degradation at doses above 100 kGy. Mainly it is attributed to oxidation reaction induced chain scission and formation of backbone scission products that was confirmed from the FTIR spectra analysis. The DTG curves of Nafion® irradiated up to 250 and 500 kGy shifted to lower temperatures demonstrating reduced thermal stability (Fig. 7b). In the DTG of Nafion® two main radiation induced changes were observed at around 357°C. Starting temperature for rapid decomposition differed by more than 10°C comparing non-irradiated polymer
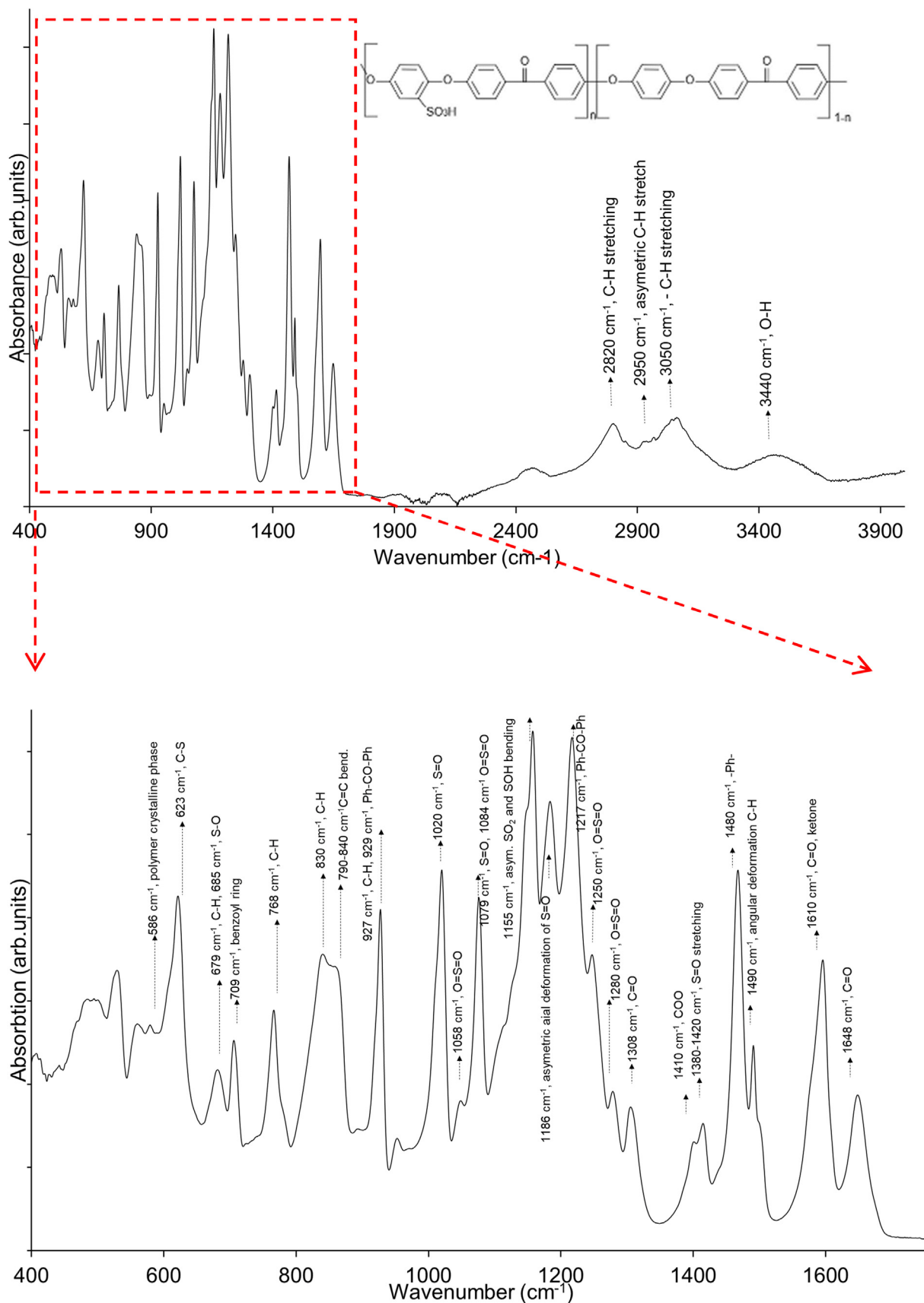
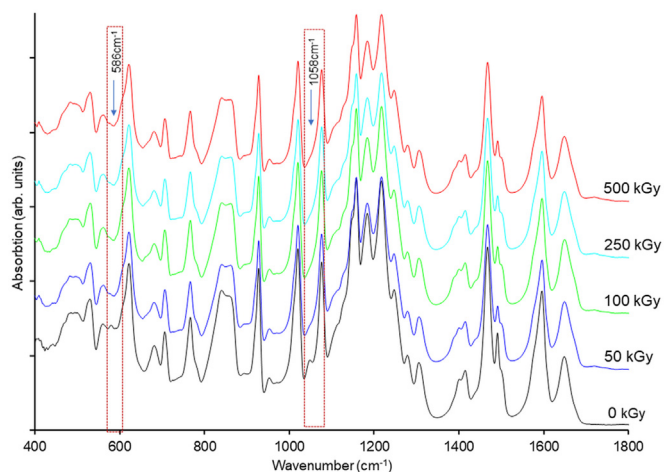**Fig. 3.** Typical FTIR spectrum of non-irradiated SPEEK tested in this study.

Fig. 4. FTIR spectra of pristine and electron beam irradiated SPEEK membranes.
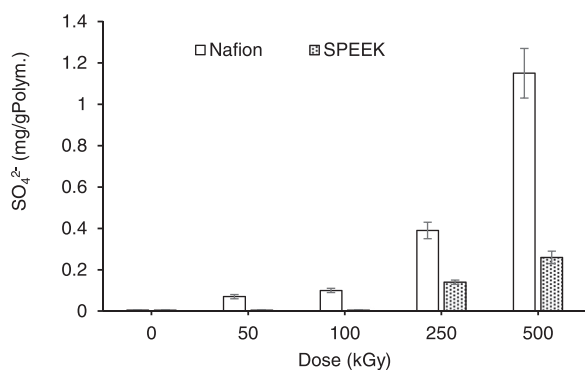

Fig. 5. Concentrations of sulphate ions in the irradiated water samples of Nafion® and SPEEK membranes.
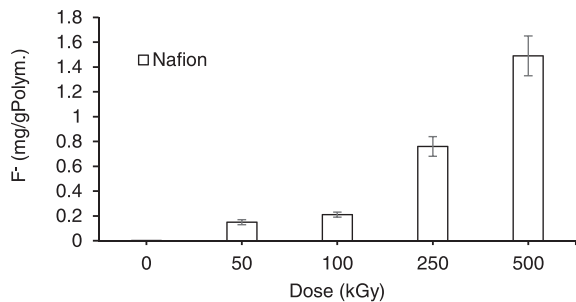

Fig. 6. Concentration of fluoride ions in the irradiated water samples of Nafion® membranes.

and polymer irradiated with 500 kGy. For the Nafion® the mass loss up to 400°C is due degradation of sulfonic groups, whereas the sharp weight loss above 400°C is due polymer backbone, decomposition of main chains. However, at doses below 250 kGy Nafion® 117 membrane expressed thermal stability up to 240°C, which make the suitable application of Nafion® membranes after low dose radiation treatment.

SPEEK demonstrated notably higher thermal stability if compared to Nafion®, which was completely degraded at 500°C. Almost 50% of the SPEEK fraction remained at this temperature. Electron beam irradiation induced transformations in the SPEEK cluster structure resulting in higher thermal stability compared to pristine SPEEK as can be seen in Fig. 8a [49]. High thermal stability is also associated with the thermal-resistance of the aromatic polyketone backbone leading to the reduction of the thermal energy. Irradia-

tion dose above 100 kGy introduced changes in the ionic clusters of the sulfonated groups leading to moderate reduction of the thermal properties. As noted in the literature [50], degree of sulfonation has notable impact of the thermal behaviour of SPEEK membrane material [51]. TGA curves of SPEEK demonstrated three decomposition regions typical to highly sulfonated SPEEK membranes (Fig. 8a).

First mass loss stage was related to the evaporation of water adsorbed to the surface of polymer (Fig. 8a). Second weight loss of about 20% at a temperature range of 300–390°C can be associated with the thermal degradation of sulfonic acid groups in SPEEK. This stage of the structure degradation was slightly affected by the electron beam irradiation. The third weight loss region at temperatures ranged between 500 and 650°C can be attributed to the exothermic degradation as a result of thermal oxidation and decomposition of the main chain of the polymer. It can be observed that increase of the irradiation dose up to 250 kGy has increased thermal resistance of the SPEEK backbone (Fig. 8b). DTG curves of SPEEK indicated several parallel processes occurring during thermal degradation above 500°C, with similar shift of the peaks to higher temperatures in case of samples irradiated up to 250 kGy. Irradiation up to 500 kGy caused reduced thermal degradation due to both radiation induced rearrangement and loss of the order in the ionic clusters of the SPEEK as a result of radiation induced crosslinking. Recent reports of electron beam effect on the graft crosslinked SPEEK in the presence of crosslinking agents have indicated benefits on increased thermal stability in case of electron beam modified SPEEK [44,52]. Mass change analysis indicated that both nonirradiated and irradiated SPEEK is thermally stable up to around 300°C and that is by at least 60°C higher temperature compared to Nafion®.

3.4. DSC thermal analysis

Typical DSC curves for nonirradiated and irradiated Nafion® and SPEEK membranes are presented in Figs. 9 and 10. Both polymers demonstrated rather different character of thermal transitions that determined different heating cycles, which were used for the characterisation of membrane materials.

As it can be seen in Fig. 9a, during the first heating cycle of Nafion® there was a sharp endothermic peak at temperature ranging between 100-180°C assigned to molecular rearrangements inside the polar clusters of the polymer [53,54]. This is commonly associated as the first glass transition followed by the second glass transition at higher temperatures. Authors of recent studies reported that the 1st glass transition is caused by the mobility of the main chain in the polymer matrix, whereas the 2nd glass transition region is attributed to the vibrations of the sulfonyl groups attached to the polymer backbone [55]. In this report, the first glass transition for Nafion® 117 was tested under similar conditions to that provided in the present study. The glass transition temperature Tg of completely dried membrane was 132°C, whereas the second glass transition associated with cluster transformations was determined at temperatures exceeding 190°C [48].

Due to the reduction of the thermal stability, second cooling and heating cycles did not provide information of 1st glass transition of Nafion®. Mainly the changes at higher temperatures were attributed to oxidation and decomposition of Nafion® backbone - CF₂ groups. That is why only the DSC curves of the 1st melting cycle were analysed.

For nonirradiated Nafion® membrane a peak centred at 170°C. At doses up to 100 kGy there was little changes in the temperature, whereas a gradual decrease from 173 to 144 and 140°C was determined with increase of the radiation dose from 100 to 250, and 500 kGy, respectively, that is associated with radiation induced oxidation and chain scission (Fig. 9b).
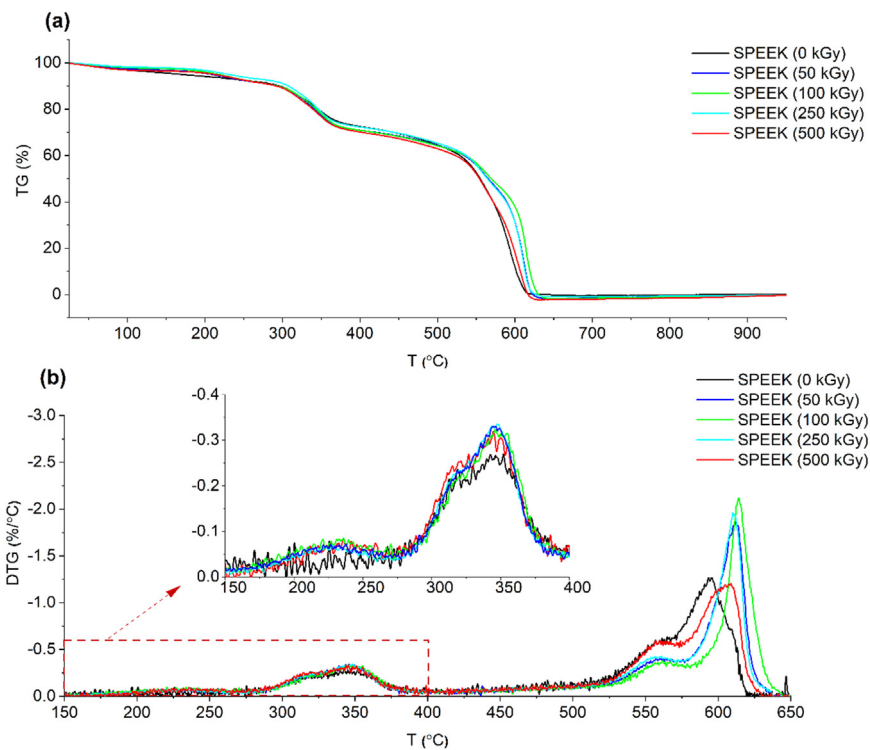
Fig. 7. TGA (a) and DTA (b) curves of pristine and electron beam irradiated Nafion® membranes.
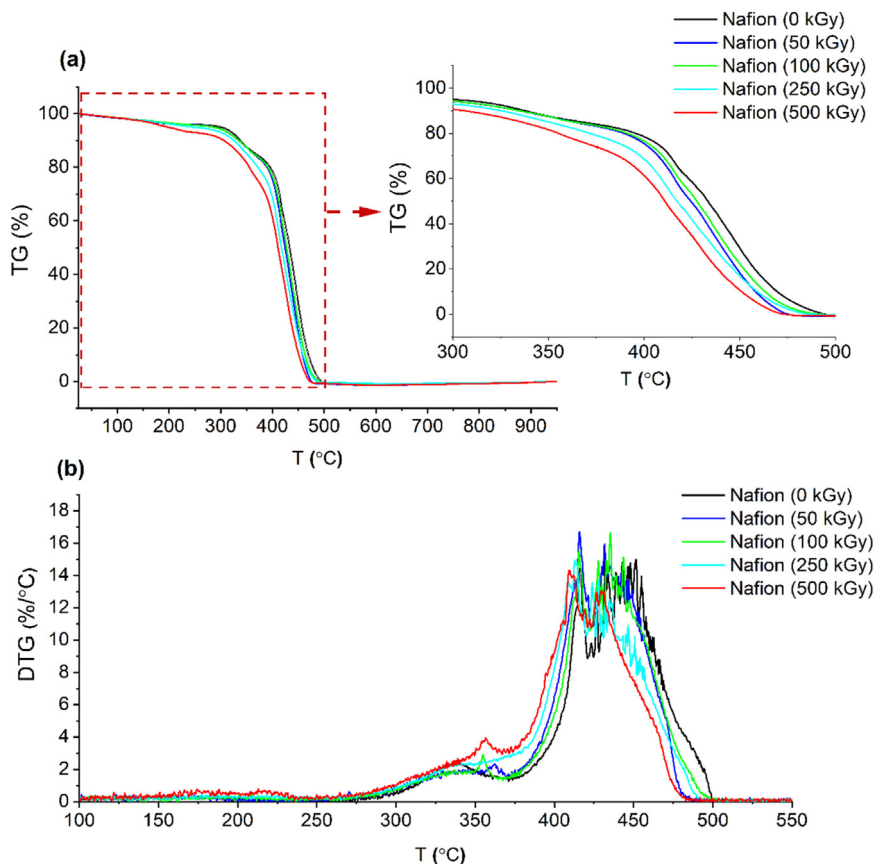

Fig. 8. TGA (a) and DTA (b) curves of pristine and electron beam irradiated SPEEK membranes.
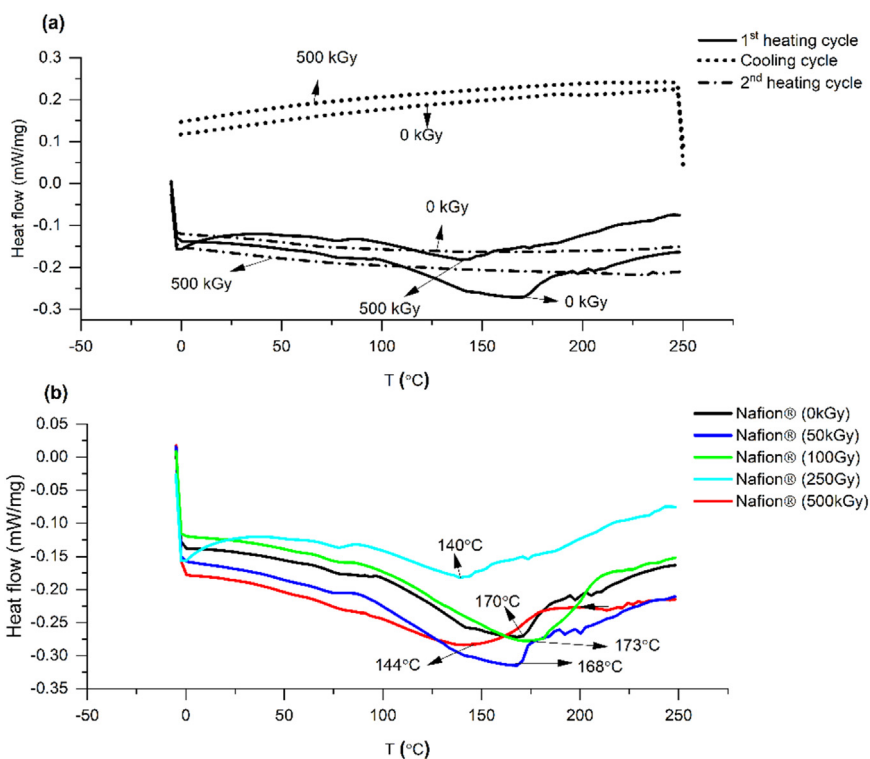
Fig. 9. Typical DSC curves of the 1st heating run, cooling run, and the 2nd heating run for pristine and irradiated at 500 kGy Nafion® membranes (a) and dose dependence of the 1st cycle transitions of Nafion® (b).
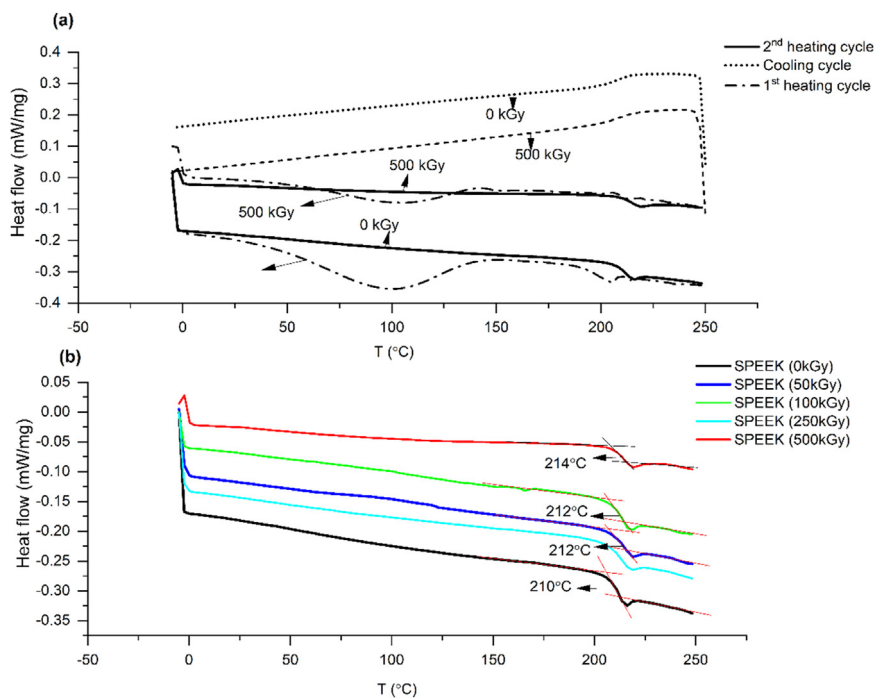

Fig. 10. Typical DSC curves of the 1st heating run, cooling run, and the 2nd heating run for pristine and irradiated at 500 kGy SPEEK membranes (a) and dose dependence of the 1st cycle transitions of SPEEK(b).

The second Tg for Nafion® was observed at 195°C and it can be associated with the strong interaction between the sulfonic acid clusters in the side chains. Formation of radiation defects and their impact on sulfonyl groups shifted thermal transitions at higher temperatures (Fig. 9b).

SPEEK DSC curves of the 1st heating cycle contained endothermic peaks determined around 100-140°C and associated with clus-

ter changes affected by the plasticisation factor of adsorbed water (Fig. 9). Due to the signal effect, only the second melting peak data were compared. The onset and the middle point glass transition temperature of pristine SPEEK was 206 and 210°C, respectively. These values were comparable to the results of other author studies [5,56].
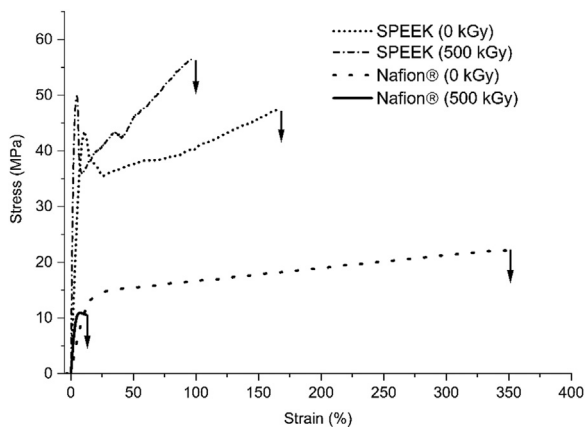
Fig. 11. Typical stress – strain curves of nonirradiated and electron beam irradiated at 500 kGy Nafion® and SPEEK membranes.

The glass transition temperature of SPEEK gradually increased with increase of the radiation dose. The onset temperature reached 209°C and the maximum temperature reached 214°C for SPEEK irradiated up to 500 kGy. That could be explained by radiation in-

duced changes in the backbone of SPEEK causing reorganisation of the crystalline phase and formation of crosslinks.

Increase of the glass transition temperature was reported as one of the indicators of radiation induced crosslinking in the case of recent studies [53].

3.5. Tensile properties

Mechanical strength properties (the modulus of elasticity, the stress at yield, tensile strength, and the elongation at break) were compared at room temperature for pristine and irradiated Nafion® and SPEEK membranes providing information about polymer properties, crystallinity, deformability characteristics and change of exploitation behaviour under the effect of ionising radiation.

Typical stress strain curves of Nafion® 117 indicated character of branched polymer with rather high deformability and acceptable strength characteristics, whereas irradiation up to 500 kGy induced notable deterioration of load endurance and rupture of the material because of Nafion® degradation (Fig. 11) that was indicated also by structure analysis and thermal analysis methods.

Stress-strain behaviour of SPEEK was characteristic to semicrystalline polymer as the crystallisation rate was notably decreased
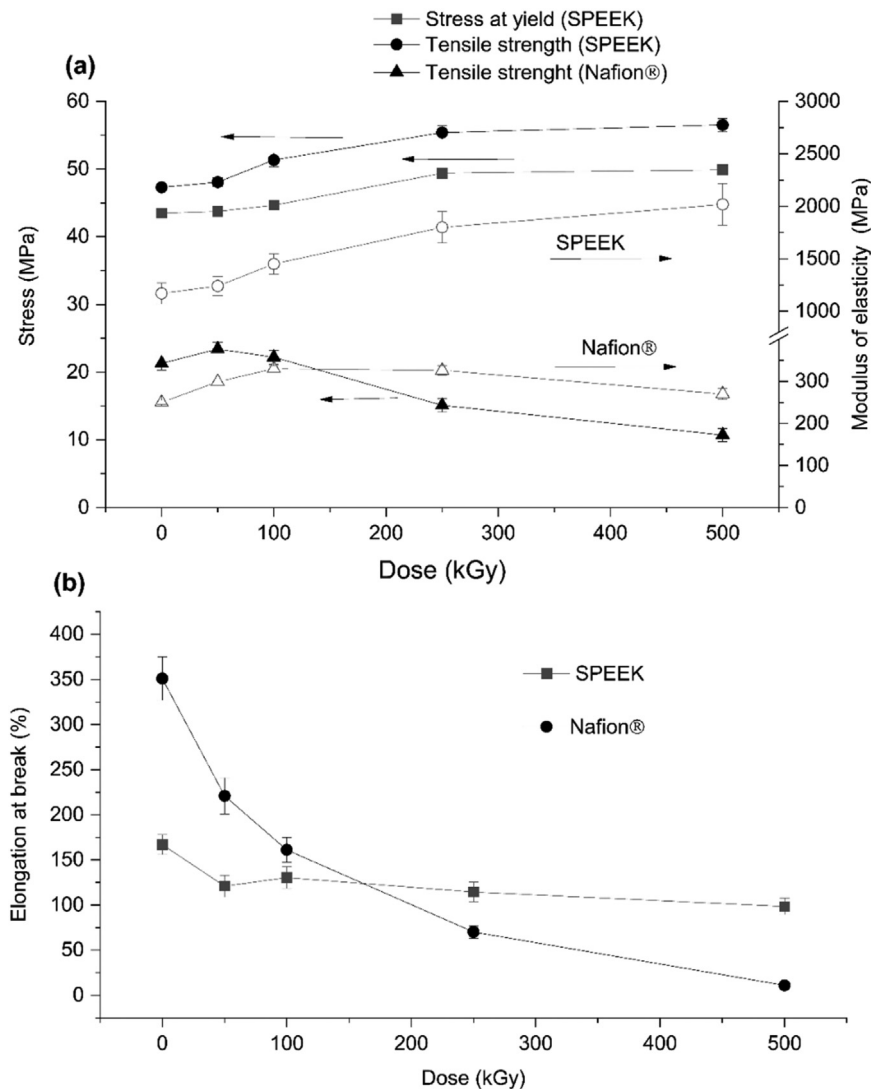

Fig. 12. Characteristic tensile strength characteristics (the modulus of elasticity, stress at the yield and the tensile strength (a) and the elongation at break (b) as dependence of the radiation dose.
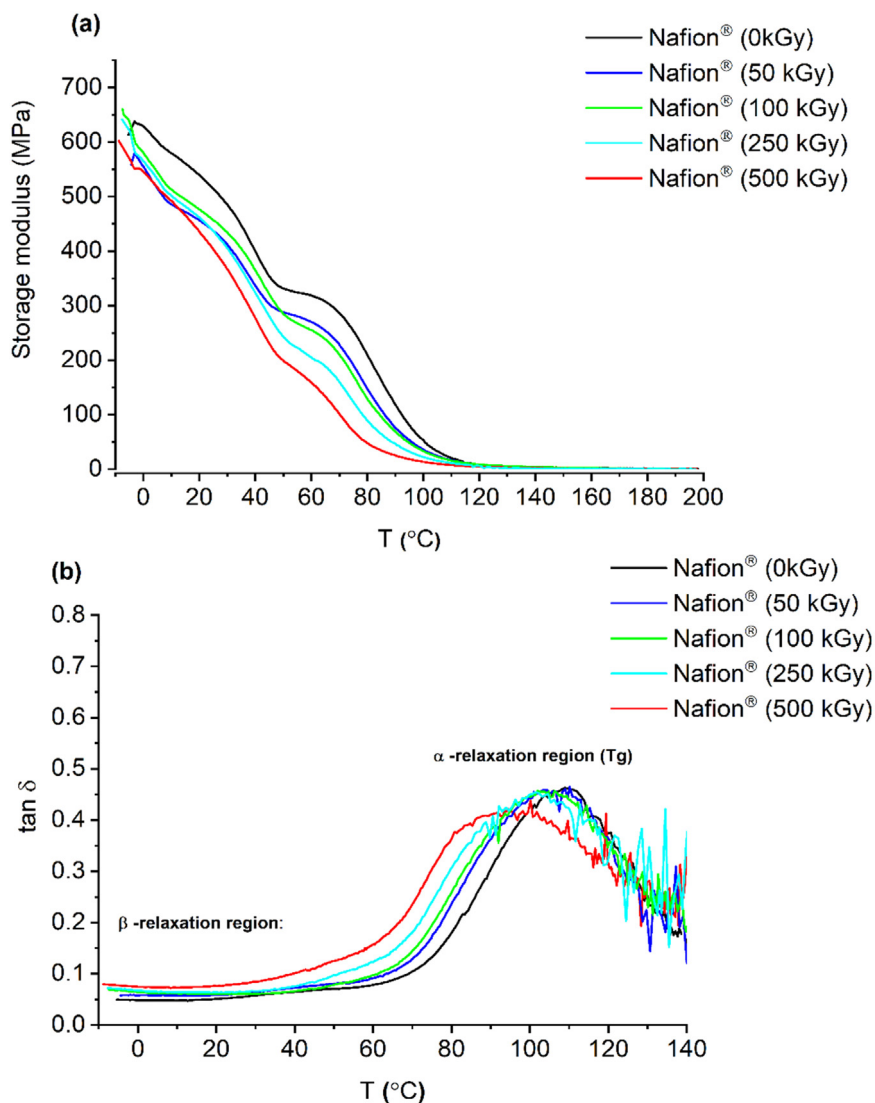
Fig. 13. The effect of irradiation dose on the storage modulus E′ (a) and tan delta (b) of Nafion® membrane materials.

due to the high sulfonation degree of the PEEK. The characteristic of the pristine SPEEK tensile characteristics with the defined stress at yield and the elongation at break were comparable with that reported in literature for SPEEK membranes with similar degree of sulfonation [57]. Stress strain curve of SPEEK irradiated up to 500 kGy indicated a notable increase of the yield stress attributed to effect on the crystalline phase due to the formation of crosslinks, that also affected strain hardening and increase of the tensile strength. Meanwhile, the elongation at 500 kGy dose remained sufficiently high that may be related to radiation tolerance of SPEEK structure compared to that of Nafion®.

Characteristic tensile properties of the irradiated membrane materials are compared in Fig. 12. These values were determined under room conditions (30% RH and 23°C temperature) and effects of the irradiation assessed. Mechanical properties of pristine Nafion® 117 coincided with the data reported in the technological data sheet as the material was a commercial membrane. As expected from the provided structure studies and thermal analysis, the increase of the dose induced degradation of Nafion®. That was also confirmed by comparing the mechanical properties of Nafion®. Deterioration of Nafion® mechanical properties was notable at these doses increasing 100 kGy material lost its deformation capacity and become brittle indicated by the decrease of the

elongation at break. Increase of the modulus of elasticity correlated with the irradiation dose. Change of the crystalline phase may be a factor causing brittle character within radiation induced degradation of Nafion® [13].

The mechanical properties of SPEEK membranes, eg., the stress at yield, tensile strength, and the elongation at break all showed similar or improved properties after irradiation to doses up to 250 kGy. Characteristic stress-strain curve, values of the modulus of elasticity and the tensile strength of pristine SPEEK membrane coincided with the characteristic values reported in other studies for SPEEK with approximately the same degree of sulfonation (74%) [5,58]. of The modulus of elasticity increased almost twice, whereas tensile strength also presented notable increase by 1.2 times comparing the SPEEK irradiated at 500 kGy and pristine membrane material. The values of the elongation break indicated slighy decrease at irradiation doses increasing up to 250 kGy due to reduced chain mobility and formation of crosslinked structure. The effect on the crystalline phase can be based on partial deterioration of sulfonic groups and formation of crosslinks that was also confirmed by FTIR.

While most of the reports attributed to electron beam irradiation of SPEEK under the effect of crosslinking additives used as secondary crosslinking promoters and linkers, in all these cases the
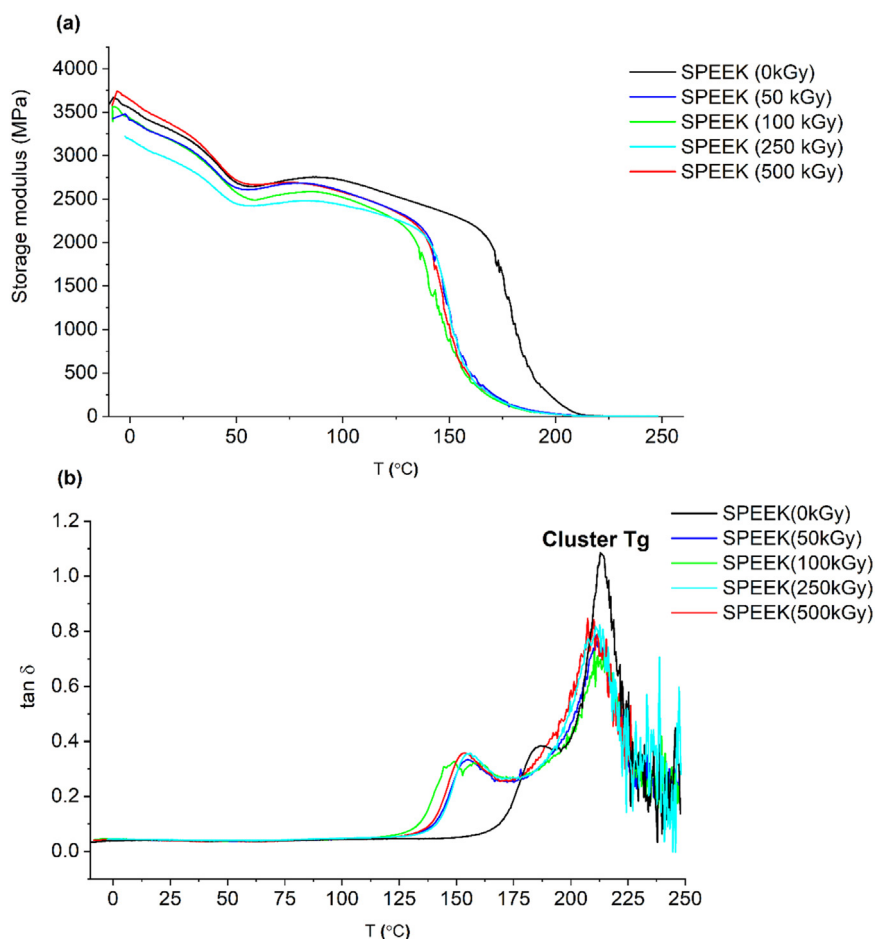
Fig. 14. The effect of irradiation dose on the storage modulus E′ (a) and tan delta (b) of SPEEK membrane materials.

effect SPEEK irradiation was the same conforming the increase of the mechanical properties as a result of radiation crosslinking of SPEEK macromolecule groups [59,60].

3.6. Dynamic mechanical analysis (DMA)

Assessment of changes of the material properties in different temperature intervals, especially at temperatures associated with glass transition temperature of Nafion® and SPEEK (Tg > 150°C and >200°C for both polymers, respectively), is also of great importance. Therefore, the DMA analysis was used to evaluate the change of the storage modulus and the damping factor (tan δ), which is the ratio of the loss modulus and the storage modulus and characterises dynamic mechanical relaxations and especially the glass transition of the polymer after their exposure to ionising radiation.

DMA data for irradiated Nafion® membranes are compared in Fig. 13a and 13b. The storage modulus decreased 1.3 times (from 515 MPa to 404 MPa) with increase of the irradiation dose. At temperatures around 80°C attributed to common application temperatures of these membranes, a notable reduction of elastic modulus was observed: the value decreases from 210 MPa to 47.5 MPa (decrease of the storage modulus up to 4.4. times) due to the chain degradation and oxidation Fig. 13a. The tan δ curve indicated two characteristic transitions of Nafion®, which are related to Tg signal shift to lower temp. due to radiation induced chain scission (difference up to 12°C).

The storage modulus of SPEEK both at room temperature and around 80°C did not show notable differences with increase of the

irradiation dose. The variations of E' values at 250 and 500 kGy reached less than 5% of that compared to pristine SPEEK (Fig. 14). The E' at temperatures > 150°C and around the Tg of SPEEK presented notable decrease with the dose after irradiation as a result of ionic cluster interactions due to the -SO$_3$H plasticizing effect leading to reduced modulus. This decrease can be associated with the radiation induced changes in structure confirmed by FTIR analysis. However, the radiation crosslinking at 500 kGy may be a reason for increase of the storage modulus as compared to changes at lower doses of irradiation [5].

Fig. 14b show the tan δ with two transitions of pristine SPEEK at 189°C and 214°C, which may be associated with the α transitions attributed to the onset of long-range mobility of main polymeric chain and pendant sulfonic acid groups.

It can be well seen that irradiation affects the SPEEK chain mobility ofleading to the transfer of the signal to higher temperatures and affecting over shifting of the polymer chains. There is new signal appearing at 154°C that could be associated with radiation induced structure reorganisation.

3.7. Ion conductivity

In previous studies the effect of DS value on the SPEEK conductivity was evaluated and the SPEEK membranes synthesized and used within this study were characterised as most optimum with rather high DS, appropriate mechanical properties and conductivity. Average ion conductivity of SPEEK that was reported in this study and confirmed also by previous results was 0.013 S/cm (Fig. 15a). In the study, where the method was reported and study
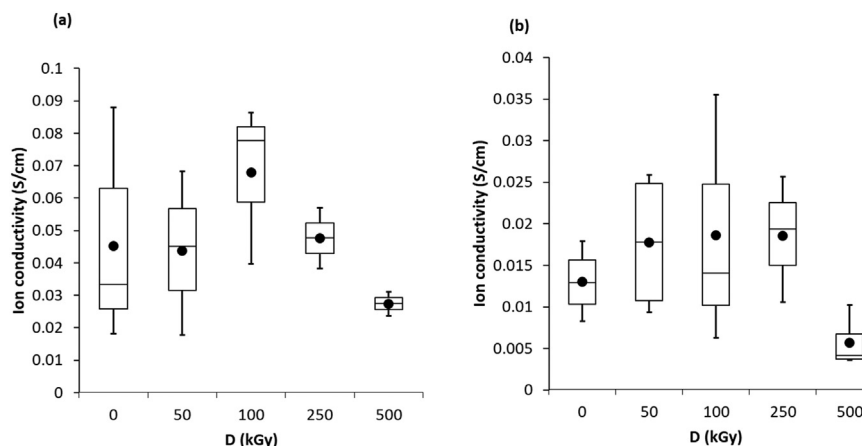
Fig. 15. Box plots characterising the dose dependence of Nafion® (a) and SPEEK (b) membranes irradiated from 0 to 500 kGy of accelerated electrons (the dot characterises the average conductivity).
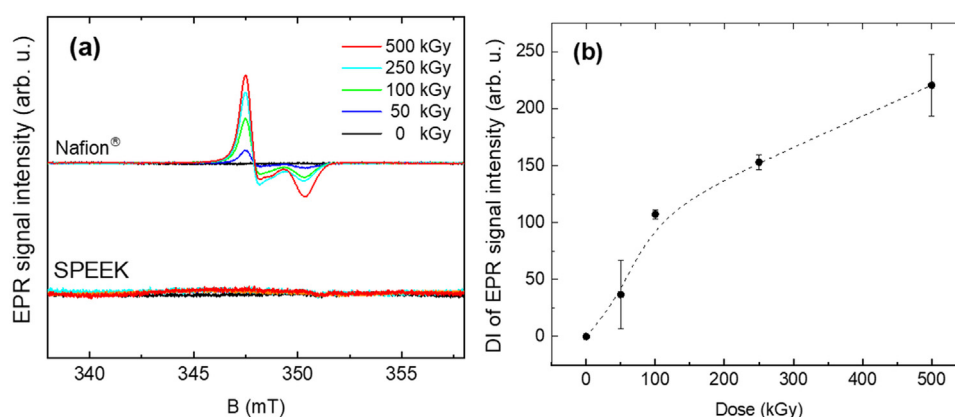

Fig. 16. EPR spectra of the investigated samples irradiated with different electron doses (a); double integral (DI) of EPR signal intensities as a function of irradiation dose for the Nafion® sample (b).

of DS was evaluated, the value was 0.011 S/cm for SPEEK with DS of 72%, respectively [31]. Comparing the box plot in Fig. 15b in can be seen that the value of ion conductivity for pristine SPEEK ranges between 0.008 and 0.018 S/cm. On average the conductivity is 3.5 times lower as the value determined for commercial fuel cell material - Nafion® possessing an average ion conductivity of 0.045 S/cm. Measured value of SPEEK conductivity coincided with the values of SPEEK membranes reported in other author studies, whereas proton conductivity reached 0.107 S/cm at 72% DS, which was increased to 0.291 S/cm at increased DS to 128% [5]. This study also reported Nafion® ion conductivity 0.018/cm at 30°C (Fig. 15a). An another study indicated Nafion® 117 membrane conductivity of 0.015 S/cm at 30°C temperature and 0.035 S/cm at 60°C and 70% RH [47].

Degradation of structure introduced slight change of proton ion conductivity of Nafion®: the average values of ion conductivity were decreased from 0.045 S/cm to 0.027 S/cm, probably due to the structure branching and oxidation.

In the case of SPEEK it was also found that radiation had little effect on the ion conductivity that remained the same on average, when comparing conductivity of pristine SPEEK and irradiated up to 250 kGy. Conductivity was notably reduced at 500 kGy that could be explained by radiation crosslinking induced changes of the structure resulting in reduced proton permeability. Increase of crystallite size can also affect mechanical and thermomechanical properties. Previous studies by other authors have indicated improvement of mechanical properties, but reduction of ion conductivity as a results of SPEEK crosslinking [44].

3.8. EPR analysis

EPR spectroscopy measurements were performed to characterize the effect of electron irradiation on paramagnetic defect formation in the investigated membranes. EPR spectra of the samples irradiated with different doses are presented in Fig. 16.

No EPR signals could be detected in the unirradiated samples. An EPR signal in the range of 346-351 mT appeared in the Nafion® samples after the irradiation. Double integral (DI) of the signal as a function of the irradiation dose is plotted in Fig. 16b and positive correlation can be observed. Similar results have been obtained in the investigations of defects generated by ionizing radiation in previous studies [61,62]. In contrast, no signals could be detected in the irradiated SPEEK samples. Therefore, the experimental results suggest a higher radiation resistance of SPEEK in comparison to Nafion®; however, it is also possible that the defects generated in SPEEK require low temperature for detection or might not be paramagnetic at all. A high resistance to ionizing radiation has previously been demonstrated in poly ether ether ketone (PEEK) polymers [63].

EPR spectra simulations were performed for a more detailed analysis of the Nafion® sample; the results are shown in Fig. 17.

The simulation was performed in an electron spin $S = 1/2$ model. The g-factor was determined to be axially symmetric with component values $g_1 = g_2 = g_\perp = 2.021 \pm 0.001$ and $g_3 = g_{||} = 2.005 \pm 0.001$. In studies of similar systems, g values in the vicinity of 2 have been attributed to peroxyl and superoxide radicals [61,64–66]
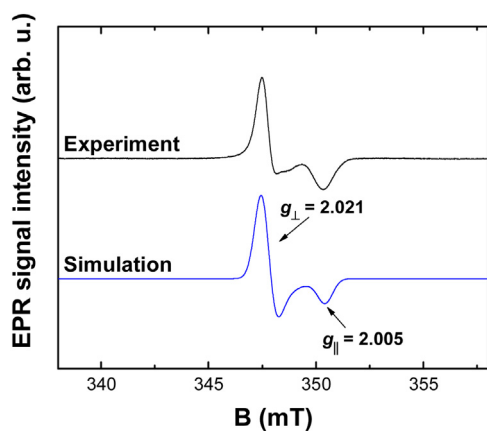
Fig. 17. Simulation of the Nafion® EPR spectrum after a 500 kGy irradiation dose.

4. Conclusions

This study presents a comparative analysis of ionising radiation effects on commercial Nafion and its alternative - sulfonated poly ether ether ketone membrane materials, which were irradiated with accelerated electrons at doses ranged between 50 kGy (around the sterilisation level of medical membrane materials) and up to 250 and 500 kGy (doses simulating the effect of few year exposure to β-radiation of tritium). The overall findings of this study suggest that the SPEEK membranes offer the possibility for improving the performance of proton exchange membrane fuel cell providing enhanced thermal, mechanical and hydration stability compared to that of commercial Nafion® membrane material. Structure analysis and detailed evaluation of thermal transitions indicated rather different processes involved in radiation induced modification of Nafion® and SPEEK. Thermal stability was notably increased as well the crosslinking introduced notable increase of strength of SPEEK at exploitation temperatures of commercial PME membranes compared to reduced performance of Nafion®. The destruction of the Nafion® backbone and its correlation with the irradiation dose is clearly demonstrated also with the fluorine anion concentration increase in the surrounding water. Dominant interaction mechanisms lead also to the differences in mechanical and thermal properties after exposure to the radiation: Nafion® demonstrates degradation of its mechanical properties, as well as decrease of the glass transition temperatures. In contrary, mechanical and thermal properties of SPEEK have improved after irradiation. Therefore, it can be concluded that SPEEK has superior radiation resistance properties.

Declaration of Competing Interest

None.

CRediT authorship contribution statement

E. Pajuste: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition. **I. Reinholds:** Conceptualization, Methodology, Investigation, Writing – original draft, Visualization. **G. Vaivars:** Conceptualization, Investigation, Resources, Writing – review & editing. **A. Antuzevičs:** Methodology, Resources. **L. Avotiņa:** Methodology, Writing – review & editing, Visualization. **E. Sprūģis:** Investigation. **R. Mikko:** Methodology, Resources. **K. Heikki:** Methodology, Resources. **R.M. Meri:** Methodology, Investigation. **R. Kaparkalējs:** Investigation.

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