



Preparation and characterization of sulfonated polyethersulfone for cation-exchange membranes

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ABSTRACT

Polyethersulfone (PES) was sulfonated by chlorosulfonic acid and then used as the polymer matrix for cation-exchange membranes (CEM). The sulfonation reaction was conducted at room temperature and the degree of sulfonation was easily controlled by varying the ratios of reaction reagents. The morphology, physical properties, electrochemical properties, mechanical and thermal stabilities of the membranes were characterized to evaluate the properties of sulfonated polyethersulfone (sPES) as a cation-exchange membrane. Membranes with 40% degree of sulfonation were found to have the optimal properties, with good water uptake, ion-exchange capacity (IEC: ~ 1.44 mequiv g^{-1}) and conductivity while maintaining excellent mechanical stability and thermal stability. These membranes can be considered as excellent candidates suitable for water desalination by electrodialysis.

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1. Introduction

A large number of ion-exchange membranes have been widely studied due to their versatile applications in food, drug and chemical industries, waste water treatment, and separation processes [1–5]. Ion-exchange membranes have also been used in electrodialysis for brackish water desalination for several decades. For the desalination application, it is essential for ion-exchange membranes to possess high selectivity and conductivity, good mechanical and chemical stability as well as resistance to organic fouling. To achieve these properties, the selection of polymeric matrices, modification of membrane using various functional groups and surface layer of membranes were utilized as strategic tools. To date, most of the ion-exchange membrane studies have been focusing on Nafion, sulfonated polystyrene and sulfonated poly(phenylene oxide) based material systems. On the other hand, polyethersulfone (PES) as a type of thermoplastic has been extensively modified and used in membrane separation applications including as a low-cost alternative to expensive fluorinated polymers in fuel cells, in ultrafiltration and RO membranes for desalination and in gas separation processes, due to its excellent mechanical, thermal and chemical stabilities [4,6–11]. However, very few works have a focus on using PES as polymer matrix for ion-exchange membrane specifically for electrodialysis application.

Although PES possesses many good characteristics, the hydrophobicity of the material often limits its application especially in desalination processes. To apply PES in desalination by electrodialysis, charged groups particularly from sulfonic acid have been introduced into the polymer chains making them ion-exchangeable. There are a number of methods to introduce sulfonate groups ($-SO_3^-$) into polymer chain of polyethersulfone [4,12,13]. In general, sulfonation reaction can be introduced pre- or post-polymerization. Though the pre-sulfonation starting from modified monomers possesses a good pathway to control the molecular structure, the post-sulfonation is more widely used due to its simplicity and low cost. Through the post-sulfonation route, some sulfonating agents such as chlorosulfonic acid, sulphur trioxide–triethylphosphate complex, and trimethylsilyl chlorosulfonate can be used in the sulfonation reaction of the polymers [4,7,12,13].

Though sulfonation reaction of PES has been well studied for a long time since the pioneering work from Noshay and Roberson group [14], there have been very limited works focusing on systematic characterization, structure–property relation and application of sPES as ion-exchange membranes [4]. Herein we report the synthesis–structure–property relationship of sulfonated polyethersulfone for use in ion-exchange membranes. Sulfonate groups were first introduced to PES by means of sulfonation reaction using chlorosulfonic acid as the sulfonating agent. Sulfonated polyethersulfone (sPES) membranes were then prepared by two different preparation conditions. To study the use of sPES as polymer matrix for cation-exchange membranes, the physical, chemical and electrochemical properties, as well as the mechanical and

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thermal stability of the membranes were also investigated in details.

2. Experimental

2.1. Materials

Polyethersulfone (RADEL A) provided by Solvay Advanced Polymers was dried at 120 °C for 24 h before use. The other chemicals were obtained commercially and were used as received without further purification.

2.2. Sulfonation reaction

PES was sulfonated with chlorosulfuric acid. In a typical procedure, 20 g of PES was dissolved in 400 g of dichloromethane under N₂ atmosphere with stirring at room temperature. Then, 15–25 cm³ of chlorosulfonic acid was gradually and slowly added to the solution. The reaction was allowed to proceed for 150 min and then was terminated by precipitating the solution into cold water. The products were filtered and washed multiple times with deionized (DI) water until pH became approximately 5–6. Finally, the sulfonated PES product dried at 120 °C for 2 days under vacuum. This sPES polymer was used as a polymer matrix for cation-exchange membranes.

2.3. Membrane preparation

Cation-exchange membranes were prepared by two different methods, the solvent evaporation and phase inversion technique. Firstly, 25 wt% polymer solution was prepared by dissolving 3 g of sPES in 9 g of N-N dimethylformamide at 60 °C for 4 h while stirring. The polymer solution was then cast on glass substrates and then either dried in a vacuum oven at 60 °C for 24 h or precipitate in DI water bath to form a membrane sheet via solvent evaporation (SE) and phase inversion (PI) method, respectively. The thickness of the membranes was controlled by means of a doctor blade. The prepared membranes were treated in hot water for 2 h and then in 1 mol dm⁻³ HCl for 24 h. After that, the membranes were rinsed with DI water and kept in 1 mol dm⁻³ NaCl solution. All the membranes were equilibrated in working solution for at least 6 h before used.

2.4. Polymer characterization

The functional groups of sulfonated polyethersulfone were investigated using Fourier transform infrared (FTIR) spectroscopy in the wave number range 4000–500 cm⁻¹. The ¹H NMR was measured using a Bruker 500 Hz at room temperature using deuterated dimethyl sulfoxide (DMSO-d₆) as the solvent. Degree of sulfonation (DS) was calculated by acid–base titration and ¹H NMR spectra.

2.5. Membrane characterization

2.5.1. Membrane morphology

Morphology and structure of the membranes were observed using scanning electron microscopy (SEM) on a JEOL 6300 electron microscope. To obtain sharp cross-sectional surface fracture the samples were cut in liquid nitrogen, then captured water was dried out in an oven at 50 °C overnight.

2.5.2. Ion-exchange capacity (IEC) and water uptake of ion-exchange membranes

Ion-exchange capacities were measured using a titration method [15]. The cation-exchange membrane was soaked in 1 mol dm⁻³ HCl. After that, the membrane was washed with

DI water to remove excess HCl and then was immersed into 1 mol dm⁻³ NaCl solution. The number of displaced protons from the membrane was determined by titration with 0.01 mol dm⁻³ standard NaOH solution using phenolphthalein as the indicator. Then the ion-exchange membrane was soaked in DI water for 24 h or more. After that, the membrane was taken out and water on the surface was wiped off with tissue paper to measure the wet weight of membrane. Then the membrane was placed in an oven at 50 °C for 10 h or until the weight of the membrane did not change any more. The dry weight of membrane was then measured. The IEC and water uptake (*U*) of membranes was calculated using Eqs. (1) and (2),

$$IEC = \frac{ab}{W_{dry}} \quad (1)$$

$$U = \frac{W_{wet} - W_{dry}}{W_{dry}} \quad (2)$$

where *a* is the concentration of NaOH solution used (mol dm⁻³), *b* is the volume of NaOH solution used (dm³), *W_{dry}* is the dry weight of the membrane and *W_{wet}* is the wet weight of the membrane.

2.5.3. Contact angle of membrane

The contact angle of water on prepared membranes was determined at room temperature using a contact angle measuring meter (OCA15 Dataphysics, Germany). At least ten angles were measured for each sample and then the average value was calculated and used in this work.

2.5.4. Electrochemical properties of ion-exchange membranes

2.5.4.1. Membrane resistance. An ion-exchange membrane was equilibrated in 0.5 mol dm⁻³ NaCl before being placed in a 2-compartment cell between platinum electrodes with effective area of 1 cm². The resistance of membranes was measured at room temperature by impedance spectroscopy (IS) using Solartron 225B in a frequency range from 1 to 10⁷ Hz with an oscillating voltage of 100 mV amplitude [16]. The resistance corresponding to the phase angle closest to zero in the Bode diagram was recorded. Then, membrane resistance (*R_{mem}*) was calculated by subtraction of electrolyte resistance (*R_{sol}*) from membrane resistance equilibrated in electrolyte solution (*R_{cell}*), according to the equation *R_{mem}* = *R_{cell}* - *R_{sol}*. Based on the electrical resistance measurement, the conductivity of membranes (*σ*, S cm⁻¹) was calculated according to Eq. (3),

$$\sigma = \frac{L}{R_{mem}A} \quad (3)$$

where *R_{mem}* is the resistance of membrane, *L* is the thickness of membranes (cm), and *A* is the effective area of the membranes (cm).

2.5.4.2. Membrane potential and transport number. Membrane potential was measured in a two compartment cell, in which a vertical membrane of 1.0 cm² effective area separated two solutions of 0.1 mol dm⁻³ KCl and 0.5 mol dm⁻³ KCl, respectively. The potential difference across the membrane was measured using a multimeter which was connected to Ag/AgCl reference electrodes.

2.5.5. Thermal and mechanical stabilities of membranes

2.5.5.1. Thermal stabilities. Thermal stability of the membranes was investigated using thermogravimetric analysis (TGA) (Mettler Teledo) under nitrogen gas flow of 20 cm³ min⁻¹ using a heating rate of 10 °C min⁻¹ in the range of 25–800 °C.

2.5.5.2. Mechanical properties. The mechanical properties of membranes were measured by means of tensile test in dry state at room temperature using an Instron 5800 at a speed of 2 mm min⁻¹. Membranes were cut into a rectangular shape with dimensions

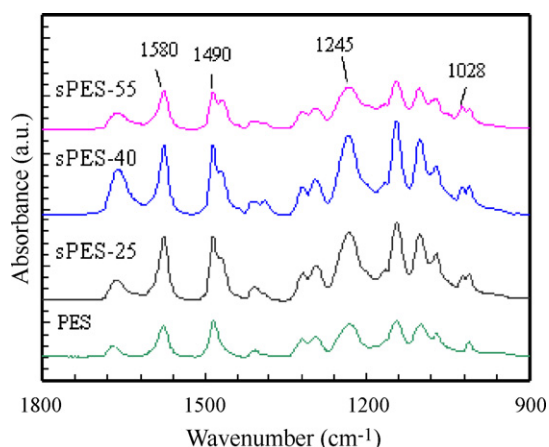


Fig. 1. FTIR spectra of polymer PES and sPES with different degrees of sulfonation.

50 mm × 5 mm. The gauge length of each specimen was 14 mm. At least five specimens from each sample were tested.

3. Results and discussion

3.1. Sulfonation reaction

In this work, PES was sulfonated by chlorosulfonic acid at room temperature in order to introduce negatively charged groups into the polymer chains. The degree of sulfonation can be easily controlled by the reaction time and the ratio of sulfonating agent and polymer materials. The presence of sulfonic acid groups (SO₃H) was confirmed by FTIR spectra (shown in Fig. 1). The numbers after the abbreviations in all figure represented the degree of sulfonation of the polymer. The peaks at 1580 cm⁻¹ and 1490 cm⁻¹ are attributed to vibration of the aromatic ring skeleton. The characteristic absorption band for the aromatic sulfone group appears at 1152 cm⁻¹ and the peak for aryl oxide appears at 1245 cm⁻¹ [17]. In sPES the adsorption peak at ~1028 cm⁻¹, which increased with the increase of degree of sulfonation, is characteristic of the aromatic SO₃H symmetric stretching vibration [17], strongly indicating the presence of SO₃H group in sPES. Note that the FTIR peak intensity of sPES-55 was weaker compared with its counterparts possibly due to the thinner sample thickness, while the characteristic peaks were still noticeable.

¹H NMR is a powerful technique used to accurately identify the chemical structure and the position of SO₃H pendent on the aromatic rings. The chemical structures of both unmodified PES and sulfonated PES are illustrated in Fig. 2. Fig. 3 shows the ¹H NMR spectra of the parent PES polymer and sPES polymer (sPES-55 is

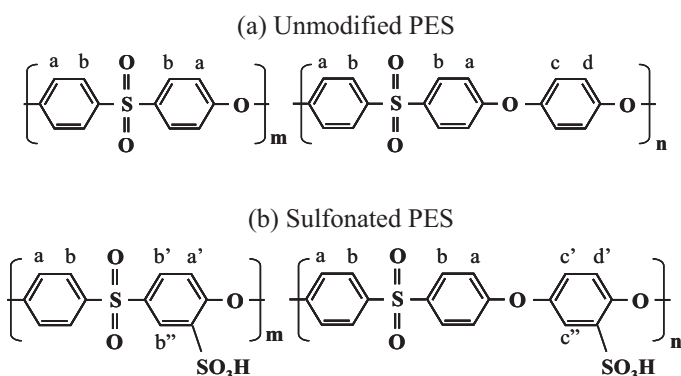


Fig. 2. Chemical structures of (a) unmodified PES and (b) sPES.

Table 1
Degree of sulfonation of the sPES.

Name	Degree of sulfonation (%DS)	
	Titration	¹ H NMR
PES	0.00	0.00
sPES-25	26.31	24.00
sPES-40	42.74	40.40
sPES-55	58.33	56.56

depicted as a representative spectrum). The presence of sulfonic acid groups on the aromatic rings led to peak shifts from 8 and 7.15 to 8.3 and 7.43 ppm, respectively.

3.2. Degree of sulfonation (DS)

The degree of sulfonation can be calculated by various methods such as IR spectra, acid–base titration, ¹H NMR and elemental analysis [17]. Herein, we calculated the DS by the titration of released H⁺ and also compared with the DS calculated from ¹H NMR, according to Eq. (4) for acid–base titration, and Eq. (5) for ¹H NMR [10,11], where the integrated area under the peak for H-b'' and H-c'' was compared with that of H-b, b'. The results are summarized in Table 1.

$$DS = \frac{0.244 [M(\text{NaOH}) \times V(\text{NaOH})]}{W - 0.081 [M(\text{NaOH}) \times V(\text{NaOH})]} \times 100 \quad (4)$$

$$DS = \frac{I(b'') + I(c'')}{I(b, b')/8} \times 100 \quad (5)$$

$M(\text{NaOH})$: the concentration of standard NaOH solution (mol dm⁻³), $V(\text{NaOH})$: the NaOH solution volume used to neutralized (dm³), W : the sample weight (g), 244: the molecular weight of PES repeat unit, 81: the molecular weight of the SO₃H group.

As can be seen from Table 1, the DS calculated from titration technique were in a good agreement with those calculated from ¹H NMR spectra.

3.3. Membrane morphologies

Membranes of various DS were prepared by two techniques and characterized by scanning electron microscopy. Fig. 4 presents the morphologies of representative membranes from both phase inversion and solvent evaporation techniques. It was clear that the membranes obtained from phase inversion were opaque, flexible and porous, while the membranes prepared with solvent evaporation method were transparent and dense. Unlike the conventional phase inversion method which generally creates asymmetric membrane imparting macro-voids in the membrane structure [12,18], the membranes prepared from evaporation methods exhibited fairly symmetric structures without any macro-voids, making the membranes mechanically robust. The properties of membrane and also the mechanical properties of the membranes related to their structure will be discussed in Section 3.6.

3.4. Properties of ion-exchange membranes

The ion-exchange capacity (IEC) provides information on the charge density in the membranes, which is an important factor related to the conductivity and transport properties of the membranes. The water uptake, ion-exchange capacity and conductivity of the membranes are summarized in Table 2. Note that E and P represent the series of membranes prepared from solvent evaporation and phase inversion method respectively.

The IEC and water uptake increased with the increase of DS due to the presence of more hydrophilic sulfonic acid groups in polymer matrix. This is consistent with the decreasing of contact angle

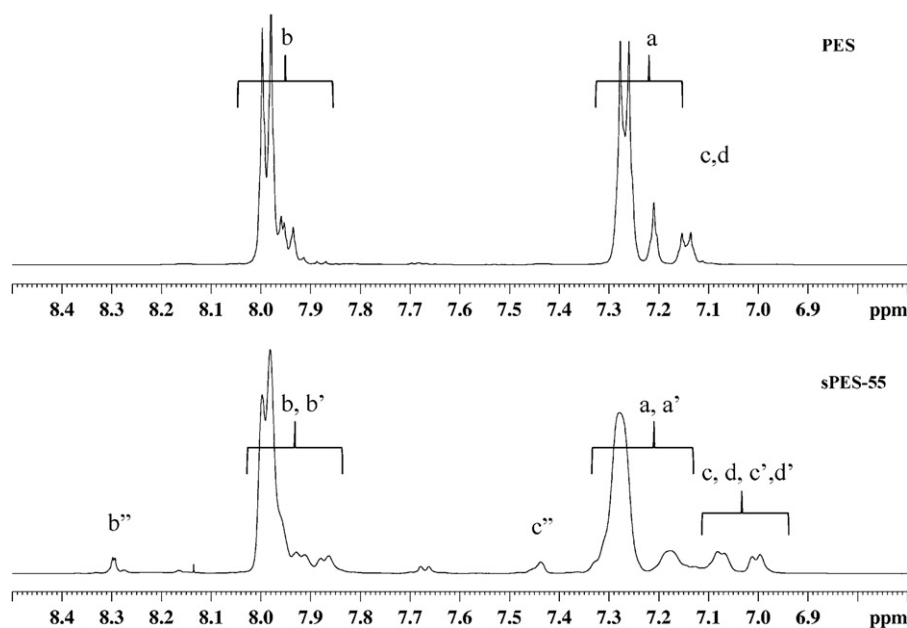


Fig. 3. ^1H NMR spectra of polymer PES and sPES-55.

of the membranes with higher DS, indicating higher hydrophilicity. The conductivity of membranes also showed a trend to increase with IEC and water uptake. Comparing membranes prepared from SE and PI techniques, due to the porous structure of membranes from PI the membranes were able to absorb more water and thus resulted in higher conductivity. Moreover, the porosity of the membranes pronounced the accessibility of the functional groups on of the polymers which in turn possessed higher IEC. However, with DS higher than 40%, sPES polymers were partly soluble in water. As the results, some soluble polymers leached out during the phase inversion process. Therefore, 40% DS membranes prepared from PI technique possessed lower IEC compared to membranes prepared from SE technique from the same DS poly-

mers. With further increased DS, for instance 55% DS in this study, we were not be able to prepare stand-alone membrane from PI method.

3.5. Transport number and permselectivity of membranes

Transport number implies the fraction of total current carried by counter ions passing through membranes [19]. The transport number can be measured by means of potential difference which is developed across the membrane when the membrane separates the electrolytes with different concentrations.

Based on the TMS approach, counter-ion transport number in the membrane phase t_i^m can be estimated by membrane potential

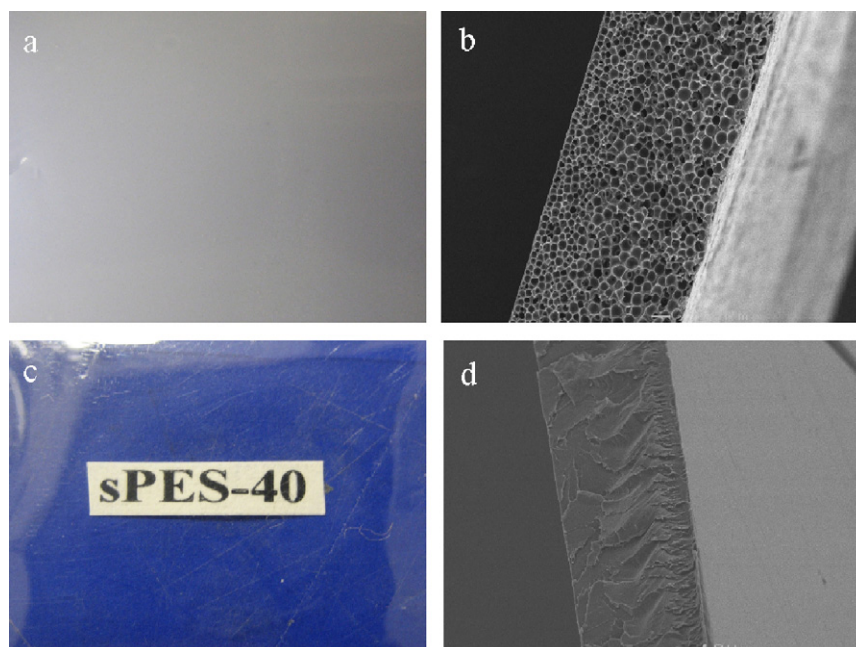


Fig. 4. Optical (a) and SEM (b) images of sPES-40 membranes obtained from phase inversion method, optical (c) and SEM (d) images of sPES-40 membranes from solvent evaporation method.

Table 2
Properties of ion-exchange membranes.

Name	Water uptake	IEC (mequiv g ⁻¹)	Conductivity (mS cm ⁻¹)	Contact angle (°)
PES (E)	3.09	0.03	0.0124	73.75
sPES-25 (E)	7.26	0.53	0.0287	67.82
sPES-40 (E)	12.54	1.44	0.0591	61.23
sPES-55 (E)	18.19	1.58	0.4237	55.42
PES (P)	72.20	0.08	0.2500	73.35
sPES-25 (P)	260.21	0.73	22.220	58.69
sPES-40 (P)	218.59	0.60	29.700	42.12

(E^m) data as shown in Eq. (6),

$$E^m = (2t_i^m - 1) \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad (6)$$

where a_1 and a_2 are the mean activities of electrolyte solutions and n is the electrovalence of the counter-ion.

Then the ion selectivity of ion-exchange membranes was quantitatively expressed in terms of membrane permselectivity, which measures how easily the counter-ion migration occurs through an ion-exchange membrane [20], as defined by Eq. (7),

$$P_s = \frac{t_i^m - t_i}{1 - t_i} \quad (7)$$

where P_s is the permselectivity of ion-exchange membrane, t_i^m is the transport number of the counter-ion in the membrane and t_i is that of the same ion in free solution at the same concentration. Both transport number and permselectivity of the prepared membranes were determined and summarized in Table 3. It was evidenced that the transport number and the permselectivity of the membranes tended to increase with increased DS in the membranes as this property depends upon the characteristic charge of the membranes [21]. However, for membranes prepared from SE, the transport number and permselectivity of the membranes dropped after peaking at 40% DS. This may be attributed to two factors. One reason is the possible leakage of the 55% DS membranes the testing cell due to its poor mechanical strength which caused co-ion species to pass through the cracks in the membranes. The other possible factor can be associated with the excessive aggregation of the ionic groups in polymer main chains forming cluster and channels for higher DS membranes. In the case of macroporous membranes prepared from PI, the membranes showed non-ion-selective property. This is not surprising as the large pores allow all ionic species passing through.

3.6. Mechanical, thermal and chemical stabilities

The mechanical properties of the membranes are shown in Table 4. When the degree of sulfonation increased, the tensile strength of the membranes slightly decreased and so did the elongation of the membranes. On the other hand, the tensile modulus was increased from 1.3 GPa to 1.5 GPa. The more sulfonic acid groups were introduced, the more rigid and brittle the membranes became. While in all cases, the mechanical properties of the membranes are strong enough for the electro dialysis application.

Table 3
Transport number and permselectivity of prepared membranes.

Name	Transport number	Permselectivity (%)
PES (E)	0.597	21.85
sPES-25 (E)	0.898	88.75
sPES-40 (E)	0.925	95.23
sPES-55 (E)	0.859	80.49
PES (P)	0.540	10.48
sPES-25 (P)	0.560	13.65
sPES-40 (P)	0.560	13.55

Table 4
Mechanical properties of membranes with varying DS.

Name	Young's modulus (MPa)	Tensile stress (MPa)	Tensile strain (mm/mm)
PES	1235.59	77.72	0.09
sPES-25	1258.11	77.61	0.09
sPES-40	1577.22	61.65	0.07
sPES-55	NA	NA	NA

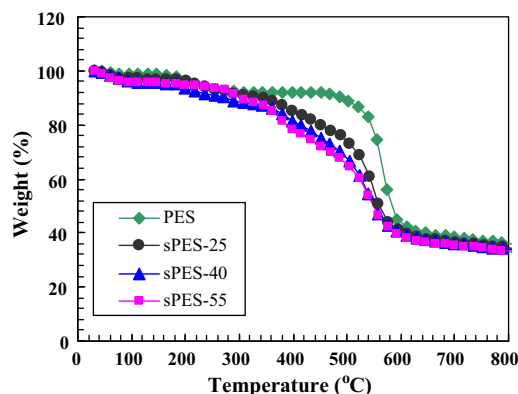
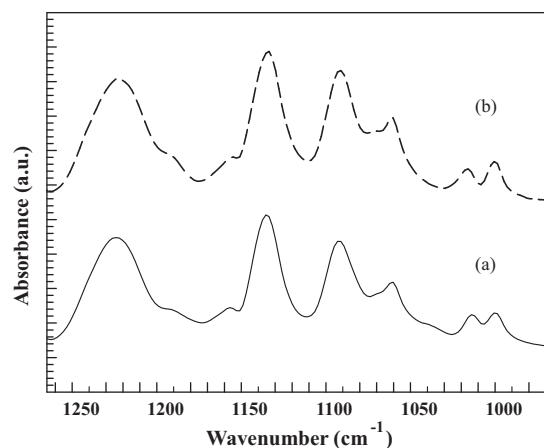


Fig. 5. TGA analysis of the prepared membranes.

Thermal stabilities of PES and sPES membranes were investigated using TGA as shown in Fig. 5. The parent PES is an excellent thermo-stable polymer which decomposes at high temperature around 500 °C. There are three steps of weight loss in the case of sPES including the loss of absorbed water at around 100 °C, the thermal decomposition of SO₃H groups [22] at 300 °C and the degradation of polymer chains near 500 °C. It can be clearly seen that the weight loss of sPES membranes at 300 °C tends to increase with the increased amount of SO₃H group introduced into the polymer chains. Considering the mild operating temperature for electro dialysis, the sPES has sufficient thermal stability to meet the requirements.

In addition, the chemical stability of sPES was investigated by FTIR technique. The IR spectra of the newly prepared sPES40 membrane and the membrane that have been stored in 0.2 mol dm⁻³ NaCl for more than 3 months were compared (see Fig. 6). It was clear that the characteristic vibrations of sPES remained nearly intact, suggesting no apparently chemical degradation from the membrane. In the meantime, we also understand that the

Fig. 6. IR spectra of (a) fresh sPES40 membrane and (b) the membrane that have been stored in 0.2 mol dm⁻³ NaCl for three months.

detailed evaluation of chemical stability on molecular levels and long term testing operation of the membranes require more systematic study which will be subjected to our further research work. Nevertheless, FTIR results suggest the negligible structural changes in the membranes in a course of three-month aging time.

4. Conclusions

Negatively charged sulfonic acid groups were successfully introduced into PES polymer via a sulfonation reaction. The sulfonation reaction was selected due to its simplicity and adaptability to the process. The charged groups introduced into the polymer chains not only improved the hydrophilicity of PES polymers, but also make them ion-exchangeable, more conductive and ion selective. The DS can be easily controlled by varying the ratio of sulfonating agents and polymer materials in this work. The IEC and electrochemical properties were proven to be strongly dependent on DS. The optimal DS for ion-exchange membrane is 40% DS, which possessed good selectivity, excellent mechanical stability and reasonable thermal stability. The newly developed sPES may be used as suitable candidates for use as polymer matrix in cation-exchange membranes for electro dialysis.

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