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Polyethersulfone sulfonated by chlorosulfonic acid and its membrane characteristics

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Abstract

Sulfonated polyethersulfone (SPES) was prepared by homogeneous method with chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. The presence of sulfonic acid groups in SPES was confirmed by ^{1}H NMR and FTIR. Thermogravimetric analysis (TGA) studies were carried out to investigate the thermal stability of SPES. Membranes were cast from SPES solutions in *N*-methyl-2-pyrrolidone. Tensile strength of prepared membranes decreased with degree of sulfonation (DS) but water uptakes of SPES membranes increased with DS. Compared with unsulfonated polyethersulfone membrane, the hydrophilicity of SPES membranes was increased, as shown by a reduced contact angle with water. Amorphous structures for SPES membranes were detected by X-ray diffraction. Atomic force microscopy phase images of the membranes clearly showed the hydrophilic domains at higher DS.

Keywords: Sulfonation; Sulfonated polyethersulfone; Chlorosulfonic acid; Membrane; Characteristics

1. Introduction

Membrane is one of the important polymer application fields. The development of new applications of membranes requires polymers with outstanding properties. As a high-performance engineering thermoplastic, polyethersulfone (PES) has high glass transition temperature, good mechanical properties, excellent thermal and chemical stability. Thus, PES is now rapidly becoming the material of choice for membrane applications. Its structure is shown in Fig. 1.

In general, a kind of material does not posses all the excellent properties required for membranes. As for PES, hydrophobicity of this material has limited its application sometimes. Therefore, polymers may need some modification to improve their performance for specific applications [1,2]. Sulfonation is a frequently used means for polymer modification to increase hydrophilicity and other membrane properties such as higher water flux, improved permeability and proton conductivity at the same time [3].

Since sulfonation is an aromatic electrophilic substitution reaction, electro-donating substituents favor the reaction whereas electron-withdrawing groups do not. Therefore, the PES is notoriously difficult to sulfonate due to the electron withdrawing effect of the sulfone linkages which deactivate the adjacent aromatic rings for electrophilic substitution. The sulfonation of PES

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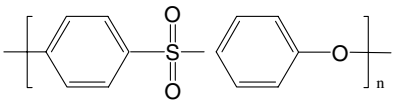

Fig. 1. Chemical structure of PES.

has been conducted in heterogeneous and homogeneous media with different sulfonating agents and solvents: SO_3/CH_2Cl_2 [4,5], $ClSO_3H/CH_2Cl_2$ [6,7], SO_3-triethylphosphate (TEP)/CH_2Cl_2 [8] and oleum/concentrated sulfuric acid [2]. Membranes made from sulfonated PES (SPES) have been studied as ultrafiltration membranes, pervaporation membranes and proton exchange membranes for fuel cells.

In the present work, we report the results on the synthesis and characterization of SPES obtained using chlorosulfuric acid as sulfonating agent and concentrated sulfuric acid as solvent, which few studies were previously conducted in literature. A series of SPES samples with different degree of sulfonation (DS) were prepared. The structure and some properties of SPES samples and resulting membranes were characterized. Here, the intended field of application of the membranes was not specified, so the membrane performances were not evaluated. The membranes were characterized in terms of mechanical properties, water uptake, contact angle, X-ray diffraction (XRD) and atomic force microscopy (AFM), which were not reported before.

2. Experimental

2.1. Materials

PES (Ultrason E6020P, M_w = 58,000 Da) was kindly provided by BASF (Ludwigahfen, Germany). The polymer was dried in a vacuum oven at 130 °C for 10 h prior to use. Chlorosulfonic acid and concentrated sulfuric acid of reagent grade were purchased commercially and used without further purification. The solvent used for membrane casting was *N*-methyl-2-pyrrolidone (NMP) of reagent grade.

2.2. Sulfonation reaction

The sulfonated polyethersulfone samples were prepared according to the following procedure. Twenty grams of PES was added to 100 ml concentrated sulfuric acid (98%) in a three-neck reaction flask, and dissolved by stirring for about 2 h at room temperature to form homogeneous solution. Chlorosulfonic acid was transferred into a dropper, then gradually and slowly added to the PES solution while stirring the solution at 800 rpm at 10 °C. The resulting reaction mixture was stirred for an additional hours. After a determined reaction time, the mixture was gradually precipitated into ice-cold deionized water under agitation, and the resulting precipitate was recovered by filtration, washed with deionized water until the pH ~6–7.

2.3. Characterization of SPES

2.3.1. NMR

The ^1H NMR (NMR-600, OXFORD) spectra were scanned to detect the occurrence of sulfonation. The solvent used to dissolve the polymer sample was deuterated dimethyl sulfoxide (d_6-DMSO). Tetramethylsilane (TMS) was used as the internal standard.

2.3.2. FTIR

The FTIR spectra of sulfonated and unsulfonated membranes were obtained using a Perkin–Elmer Spectrum One FTIR spectrometer with membrane samples.

2.3.3. Ion-exchange capacity determination

The ion-exchange capacity (IEC) can be calculated from the DS, which was determined via titration. A known amount of dry polymer (about 0.5 g) was solved in 10 ml *N*,*N*-dimethylformamide (DMF), the released amount of H^+ was then determined by titration with a standard NaOH solution using phenolphthalein as indicator. The following equations were used to calculate the DS and IEC:

$$\mathrm{DS} = 0.232M(\mathrm{NaOH}) \times V(\mathrm{NaOH}) / [W - 0.08M(\mathrm{NaOH}) \times V(\mathrm{NaOH})] \times 100\%$$

$$\mathrm{IEC} = 1000\mathrm{DS}/(232 + 81 \times \mathrm{DS})$$

where M(NaOH) was the concentration of standard NaOH solution (mol/l), V(NaOH) the NaOH solution volume used to neutralize (ml), W the sample mass (g), 232 the molecular weight of PES repeat unit and 81 the molecular weight of the $–SO_3H$.

In addition to titration, ^1H NMR spectroscopy can also be used to determine the DS.

2.3.4. Thermogravimetric analysis

The thermogravimetric analysis (TGA) spectra of PES and SPES were obtained on Perkin–Elmer TGA7 analyzer, from room temperature to 600 °C heated at 20 °C/min in nitrogen gas.

2.4. Membrane preparation

The SPES was first dissolved in NMP to form a 20 wt% solution, which was then cast onto a flat glass with a casting knife at room temperature. To obtain dense membrane, the membrane was dried in an oven step by step at different temperatures to control the solvent evaporation rate. The temperature of the oven was

programmed to remained at 40 °C for 4 h, subsequently increased to 60 °C and maintained at this temperature for 2 h, and finally the temperature was increased to 90 °C and kept constant for another 4 h. After this treatment, the membrane still contained NMP for it had higher boiling point of 204 °C Therefore, the membrane was placed in a vacuum oven for more than 2 days at 100 °C [9]. The membranes with thickness ranging from 40 to 100 μm were obtained by varying distance between the knife and the plate during the casting process.

2.5. Mechanical properties measurements

Mechanical strength of the membranes was measured by AG-10kNG Shimadzu testing machine (Japan) with an operating head load of 1 kN. Cross-sectional area of the samples was calculated. The membranes were then placed between the grips of testing machine. The grip length was 5 cm and the speed of testing was set at the rate of 5 mm/min. Tensile strength was calculated according to:

$$\text{tensile strength } (\text{N/mm}^2) = \text{max load } (\text{N}) / \text{cross-sectional area } (\text{mm}^2)$$

At least three specimens were tested for each composition and then averaged.

2.6. Water uptake

All polymer membranes used were vaccum dried at 100 °C before testing. The sample membranes were soaked in deionized water at room temperature for 48 h. The liquid water on the surface of wetted membrane was removed using tissue paper before weighing. The water uptake content was calculated by

$$\text{uptake content} = [(w_{\text{wet}} - w_{\text{dry}})/w_{\text{dry}}] \times 100\%$$

where w_{wet} and w_{dry} were the masses of dried and wet samples respectively.

2.7. Contact angle measurements

The contact angles of water on SPES membranes were determined at room temperature with a Krüss processor tensionmeter K12 (Germany) according to the plate method. At least five angles were measured and averaged for every sample.

2.8. X-ray diffraction

XRD patterns of the PES and SPES membranes were obtained on a Rigaku X-ray Automatic Diffractometer D/max-IIIc (Japan) in a continuous scan with a step size of 2θ equal to 0.02° and scan speed of 5 °/min between 2θ equal to 8° and 35°.

2.9. Morphology

AFM phase images were obtained using a Digital Instruments NanoScope IIIa scanning probe microscope (USA). Tapping mode of AFM (TM-AFM) in air was used to investigate the membrane surface morphology. All samples were dried at 100 °C for 24 h under vacuum conditions.

3. Results and discussion

3.1. Sulfonation reaction

As mentioned above, only three sulfonating agents could be used to conduct the reaction: oleum, $ClSO_3H$, SO_3 or its complexes. The choice of $ClSO_3H$ was due to its simplicity and adaptability though using it readily caused side reactions occurring [10]. But, if the reaction is carried out under suitable condition, side reaction could be suppressed to a large extent [11]. In this work, sulfonation was conducted at lower temperature (10 °C), and $ClSO_3H$ was added slowly drop by drop. The DS can be controlled by reaction time and $ClSO_3H$/PES ratio. A series of SPES samples with different DS had been prepared, including samples with DS high enough that can dissolve in hot water.

3.2. NMR

In order to determine the sulfonation site and the DS values, PES and SPESs were characterized by ^{1}H NMR spectroscopy. As shown in Fig. 2, the presence of a

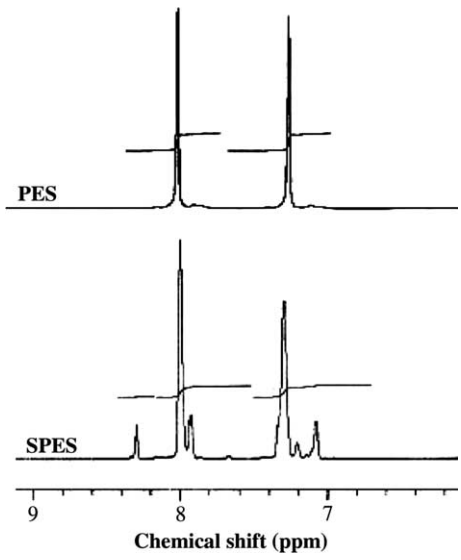

Fig. 2. ^{1}H NMR spectra of PES and SPES.

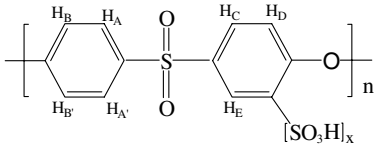

Fig. 3. Chemical structure and atom numbering of SPES, x = DS.

sulfonic acid group causes a significant down-field shift from 7.3 to 8.3 ppm of the hydrogen located in the σ-position at the aromatic ring (H_E, Fig. 3). This was in good agreement with results described in literatures [5,6,8].

3.3. FTIR

FTIR spectra were also used to confirm the pendant SO_3H group on the polymer chain. Fig. 4 shows the spectra of the parent PES and SPES. In comparing these spectra, one can see that in addition to the predicable absorption peak at $\sim$3420 cm^{-1} due to the stretching of the hydroxyls of sulfonic acid groups, the SPES absorption peak at $\sim$1025 cm^{-1} is characteristic of the aromatic SO_3H symmetric stretching vibrations. It has been known that the asymmetrical stretching vibrations of sulfonic acid groups appear at $\sim$1180 cm^{-1}, but we could not readily observe it due to near overlapping absorbances [6]. However, it still can get conclusion that the sulfonic acid groups has been introduced into the polymer chains.

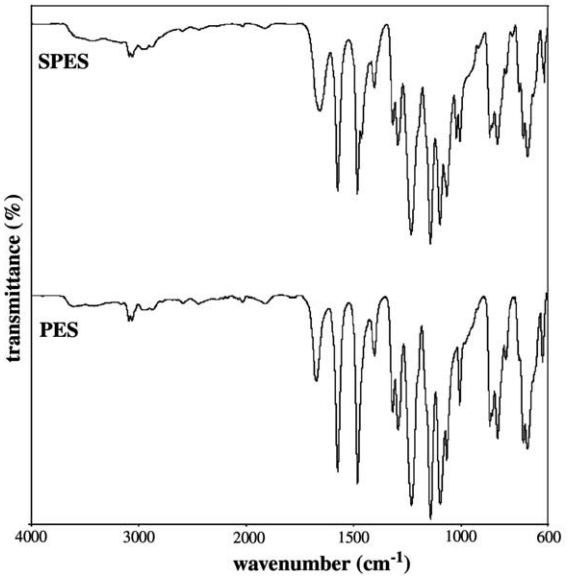

Fig. 4. FTIR spectra of PES and SPES.

Table 1
DS and IEC of some SPES samples

DS from titration (%)	9.16	14.10	24.93	29.47	43.07
DS from ^{1}H NMR (%)	8.49	11.93	25.17	30.77	41.76
DS: average value (%)	8.83	13.02	25.05	30.12	42.42
IEC: average value (meq/g)	0.37	0.54	0.99	1.17	1.59

3.4. Determination of IEC and DS of SPES

The DS was determined quantitatively via the titration method and ^{1}H NMR spectroscopy [12,13]. The ^{1}H NMR method was on the basis of comparison the peak area of the H_E signal (AH_E) with the peak areas of all the other aromatic hydrogens signals ($\Sigma AH_{A,A^1,B,B^1,C,D}$). The following equation showed the mathematical expression:

$$DS/(8-2DS) = AH_E/\Sigma AH_{A,A^1,B,B^1,C,D}$$

Good agreement was found between the values as shown in Table 1. For convenience, DSs mentioned following were all from titration.

3.5. Thermal properties

The thermal stabilities of the SPESs were determined by TGA. Fig. 5 shows the degradation curves. The parent PES was a thermostable polymer, of which the 5% weight loss temperature was nearly 550 °C and there was only one sharp weight loss that was ascribed to the decomposition of polymer main chain. For the SPESs, three transitions of loss in weight in three separate temperature ranges can be seen in TGA curves. The first, around 100 °C is related to the desorption of water bonded to the sulfonic groups. The second one occurs at around 400 °C and could be ascribed to the

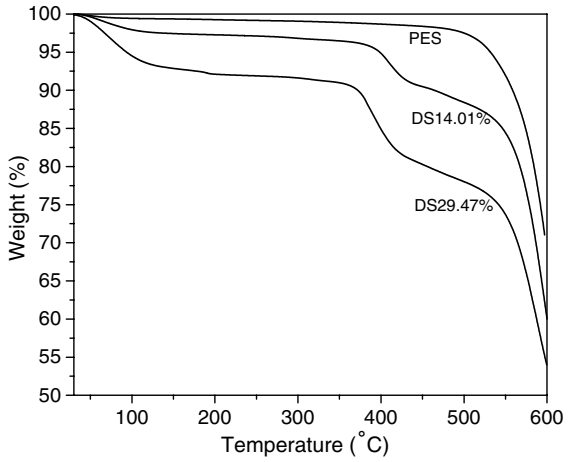

Fig. 5. TGA traces of PES and SPES.

decomposition of the sulfonic acid groups. The third thermal degradation of SPES at about 490 °C was assigned to the degradation of the polymer main chain. In addition, SPESs with higher DS lost weight more quickly. Moreover, sulfonate samples show lower decomposition temperatures with respect to PES. This difference could be explained by an enhanced asymmetry in the polyethersulfone structure due to the introduction of SO_3 groups that renders it less regular and then less stable [14].

3.6. Tensile strength

The tensile strength at break of PES and SPES is given in Table 2, it can be seen that there is a decrease in the tensile strength of the polymers after sulfonation. This reduction related to the DS might have arisen from two factors: the introduction of strong polar sulfonic acid in the polymer chain decreased the aggregative state and sulfonation caused the polymer matrix to expand thereby increasing the chain movements and then making the plastic material flexible [15].

3.7. Water uptake

It has been known that water sorption depends on the extent of sulfonation, hence higher the DS, greater the water uptake. From Table 3 it can be observed that there was nearly no water absorption when DS was low [16], but when DS reached to some extent, the water uptake increased significantly. The molecular structure of SPES was composed of a hydrophobic backbone and hydrophilic sulfonic acid groups, and the hydrophilic ion clusters were principally responsible for the water-uptake of the polymer [17,18]. The results indicated that for low-DS SPES, the hydrophilic part was isolated in the continuous hydrophobic phase. When DS reached a certain value, the hydrophilic ionic domains, became continuous and formed large channels [19,20]. It can also interpret when DS was high enough, the polymer was completely soluble in water for absorbed water promoted the phase separation.

Table 2
Tensile strength of PES and SPESs

DS (%)	0	7.22	14.10	24.93	25.27	43.07
Tensile strength (N/mm^2)	74.64	72.07	64.88	59.92	55.01	36.62

Table 3
Water uptake of SPESs

DS (%)	14.01	23.73	29.47	41.22
Water uptake (%)	0.86	5.17	6.08	17.41

Table 4
Contact angle of SPESs with different DS

DS (%)	0	14.01	23.73	29.47	41.22
Contact angle (°)	75.9	73.3	64.5	60.2	36.6

3.8. Contact angle measurements

Contact angle is the measure of surface hydrophilicity of materials. As shown in Table 4, the contact angles decreased with increasing DS, indicating an increase in hydrophilicity of the membrane [21].

3.9. XRD

In Fig. 6, the XRD patterns of SPES were reported. Typical of amorphous polymers without any crystallinity were found [22]. The analysis of the XRD spectra of PES and SPES membranes is shown in Table 5. The spectra were compared in terms of peak position, peak width, peak intensity and d-space. The peak intensity decreased with increasing DS, indicating a less order

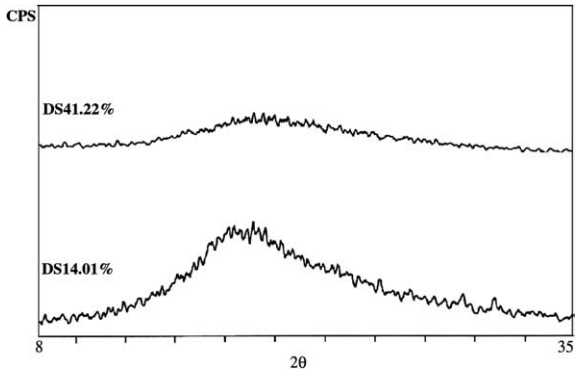

Fig. 6. XRD spectra of SPES membranes.

Table 5
Analysis of the XRD spectra of PES and SPES membranes

DS (%)	Peak position ($2\theta°$)	Peak width ($2\theta°$)	Peak intensity (CPS, counts per second)	d-Spacing (Å)
0	18.780	0.390	357	4.7213
14.01	18.920	0.270	313	4.6866
23.73	19.260	0.420	218	4.6047
29.47	18.720	0.330	214	4.7363
41.22	18.940	0.240	127	4.6817

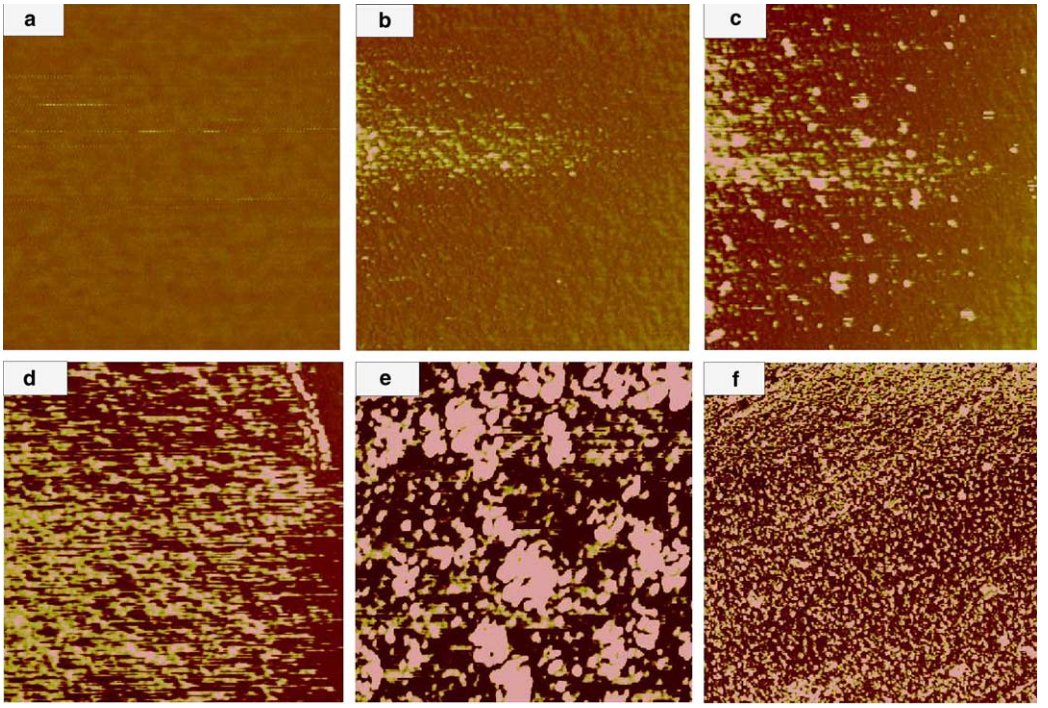

Fig. 7. TM-AFM phase images for PES and SPES: (a) PES (1 μm × 1 μm); (b) DS14.01% (1 μm × 1 μm); (c) DS23.73% (1 μm × 1 μm); (d) DS41.22% (1 μm × 1 μm); (e) DS43.07% (1 μm × 1 μm) and (f) DS43.07% (10 μm × 10 μm).

of macromolecular orientation within the polymer. The peak width was not accurate, especially for overlapped peaks. The other parameters of the peaks did not have significant change and some variation could be attributed to the differences in the thickness of samples [23,24].

3.10. Morphology

AFM was employed to explore the morphological characteristics of the SPES. TM-AFM is powerful because it can distinguish areas with different properties regardless of their topographical nature [10].

Tapping mode phase images of PES and SPES were recorded under ambient conditions on different size scale in order to investigate ionic clusters for SPES (Fig. 7). The aggregate size and connectivity was shown to be dependent on the DS. For unsulfonated PES and SPES with lower DS, featureless phase morphology was observed. On the other hand, for the SPES with higher DS, cluster-like structure was clearly visible in the phase image. For phase images of (d), the hydrophilic ionic domain began to became co-continuous to form channels of an ionic rich phase. The cluster-like structure was assigned to a softer region, which represents the hydrophilic sulfonic acid groups [10,18]. Based on the phase images of (d) and (e), it can be concluded that the SPES has a percolation limit at about 40% of DS. This percolation limit can also explain the sudden increase of water uptake.

4. Conclusions

Sulfonation of polyethersulfone (PES) was conducted with chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. A series of SPES samples with different DS were prepared and characterized. The sulfonation of SPES was confirmed by ^{1}H NMR and FTIR. As the DS of SPES increased, the decomposition temperature of polymer chains decreased. Membranes prepared from SPESs showed a decrease in tensile strength as DS increased. Compared with PES, both the hydrophilicity and water uptakes of SPES membranes increased with DS. X-ray diffraction patterns showed amorphous structures for SPES membranes and the peak intensity decreased with increasing DS. AFM phase images showed hydrophilic ionic domains connected to produce a co-continuous morphology at higher DS. There may exist a percolation limit at about 40% of DS, which was consistent with the sudden increase of water uptake. Results of this study should prove to be useful for specific application, especially as promising proton exchange membranes for fuel cells. Further studies on the SPES

membranes will investigate its performances in fuel cells applications.

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