Sulfonated polyetherketone (SPEK-C) films investigated by positron annihilation lifetime spectroscopy and atomic force microscopy

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Abstract The characterization of sulfonated polyetherketone (SPEK-C) films was investigated by using positron annihilation lifetime spectroscopy (PALS) and atomic force microscopy (AFM). It was found that free volume radius and intensity depend on the variation of sulfonation degree and solvent evaporation time of the films. Pore size and distribution determined from PALS and AFM measurements showed reasonable agreement.

Key words Atomic force microscopy (AFM), Sulfonated polyetherketone (SPEK-C), Sulfonation degree, Positron lifetime, Free volume, Pore size

CLC numbers O63, O571.3, TH742

1 Introduction

Membrane systems have been widely used in industrial applications. The free volume concept is extensively adopted in polymer science. Many properties can be explained successfully at microscopic structural level and related to macroscopic properties. PALS is one of the most sensitive techniques to study subnanometer size holes and concentration of free volume holes (cavities).[1,2] AFM has also widely been used to obtain topographical images by scanning with a sharp tip over the surface without special sample preparation since its invention in 1986.[3,4]

In the present study, the effect of sulfonation time and evaporation time were investigated in SPEK-C films. Free volume size and distribution were measured by PALS and AFM.

2 Experimental

2.1 Materials

Phenolphthalein polyether ketone (PEK-C) was a conventional polymer purchased on the market. Concentrated (w=98%) fuming sulfuric acid ($w(SO_3)$= 20%), dimethylformamide (DMF), and other chemicals were obtained commercially and used without further purification. All chemicals used in the experiments were analytically graded.

2.2 Sulfonation of PEK-C

The sulfonation method has been reported in several studies.[5-7] The mixture of polymer and concentrated sulfuric acid was stirred to achieve a certain sulfonation degree. The degree of sulfonation was determined via a combination of acid-base titration and gravimetry, and was controlled by the reaction time. The final solution was washed with iced water until the pH was nearly 7, and the obtained SPEK-C was subsequently dried at room temperature. Finally, three different kinds of sulfonation degrees of SPEK-C were obtained for the membrane preparation.

2.3 Membrane preparation

The membrane preparation was the same route

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analogous.[8] Binary solutions were prepared through the dissolution of SPEK-C of different sulfonation degrees in strong polar aprotic solvent DMF overnight at room temperature so that PES could dissolve sufficiently. The mixtures were stirred in a required time, and air bubbles were extracted through vacuumization to form casting solutions.

At room temperature, these viscous solutions were cast onto glass plates with a proper glass knife to form thin films with the thickness of about 1.5 mm. They were then immediately immersed in iced water to precipitate the polymer and for the formation of membranes. Furthermore, series of films were made from the viscous solution of 1 h sulfonation time within different evaporation time. Finally, the membranes were pretreated with 1mol/L HCl and 1mol/L NaOH solutions four times, and washed with deionized water for a further evaluation of the membrane properties.

2.4 PALS analysis

The positron lifetime measurements were carried out by using an automated EG&G Ortec fast-fast coincidence system having a time resolution of 250 ps (FWHM for the ^{60}Co prompt γ-rays). The activity of the positron source (^{22}NaCl embedded between two 1.08 mg•cm^{-2} kapton foils) was 1.11 MBq. The sample-source assembly was inserted in the usual sandwich configuration. The lifetime spectra with about 10^6 integral counts, were recorded at (298±0.5) K and fitted by applying a version of PATFIT.[9] The lifetime for pick-off annihilation can be estimated by multiplying the basic rate for $e^+e^-\rightarrow 2\gamma$ at the low energy by the probability for the positron in the positronium for finding an electron with opposite spin in the surrounding matter. The spectra were deconvoluted into three components with lifetimes τ_i and intensities I_i. Subscripts i=1-3 are ascribed to p-Ps, free e$^+$ and o-Ps respectively. By a simple model, the measured o-Ps, lifetime, $\tau_{\text{o-Ps}}$, depends on the radius of the free volume hole R according to the semi-empirical relation:[10,11]

$$\tau_{\text{o-Ps}} = [\lambda(1-\frac{R}{R+\Delta R}+\frac{1}{2\pi}\sin\frac{2\pi R}{R+\Delta R})]^{-1} \quad (1)$$

where λ=2ns^{-1} is the spin averaged Ps annihilation rate and ΔR=1.656 Å[12] is the thickness of homogeneous electron layer which is valid for polymers and containing simple covalent bonds. In this model the free-volume holes are assumed to be infinite spherical potential wells of radius $R_0=R+\Delta R$.

The volume of the free-volume hole V_F (in Å^3), for a spherical hole can be calculated by

$$V_F = \frac{4\pi R^3}{3} \quad (2)$$

where R can be obtained from Eq.(1). The relative fractional free-volume (%) is expressed as Ref.[13]:

$$f_v = CV_F I_3 \quad (3)$$

where V_F is the free-volume of the membrane and I_3 is the intensity corresponding to τ_3. The scaling factor C is obtained from the variation of free-volume with temperature.

2.5 AFM analysis

AFM is a powerful tool in characterizing membranes as it allows determination of surface morphology and surface pore size distribution with no special sample preparation. All the samples were scanned using XE-100 atomic force microscopy made by PSIA.[14] Membrane morphology was measured in air with a scan rate of 1Hz at 256×256 resolution in contact mode. During the scan process, the setpoint was kept at 0.9 nN so that the tip gently touched the surface of the sample. The scan range was 10μm×10μm. Among the scan results, the topography image of 1c could not be obtained because the surface of 1c was too rough for AFM scale.

3 Results and discussions

3.1 Membrane characterization by AFM

AFM was used to investigate the shape of pores or cavities on the surface as well as the roughness of the skin when the coagulation conditions were varied. The results of 3 h-sample are shown in Fig.1. The topography image shows some ditches on a rough surface. The ditches are about 50 nm in depth and 1.2 μm in width. There was no apparent hole on the surface.

The results of 1a-sample are shown in Fig.2(a). The topography image shows that the surface seems a less rough than that of the 3 h-image. Apparently different from 3 h-sample, there were about 20 holes in 10μm×10μm area. The depth and diameter of the holes can be read, as shown in Fig.6. The depth was different with the deepest about 550 nm in depth and about 1 μm in diameter. On average, the depth of the holes was about 200 nm and the diameter about half to one micron.

The results of 1b-sample are shown in Fig.3. There were less than 10 holes in 10μm×10μm area. As shown in Fig.6, each of them was about 280nm in depth and about 1.3μm in diameter.

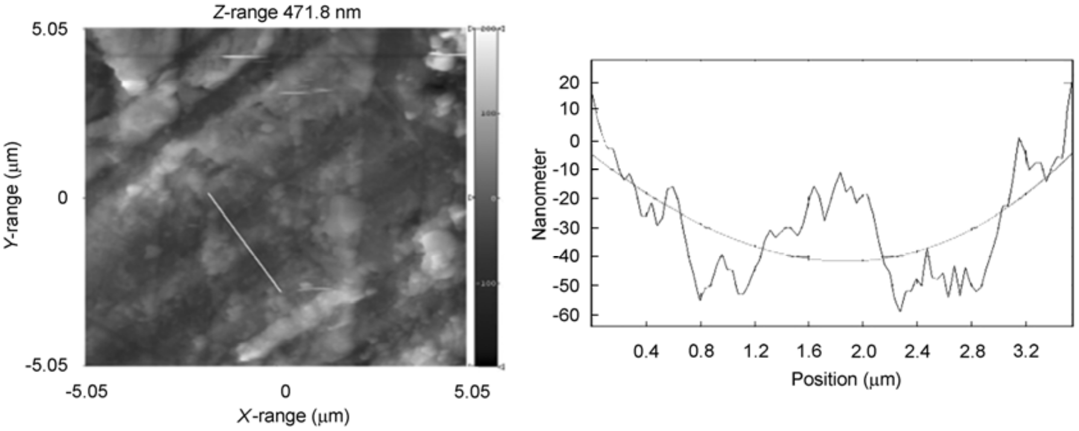

Fig.1 A top view and line profile of 3 h-sample surface.

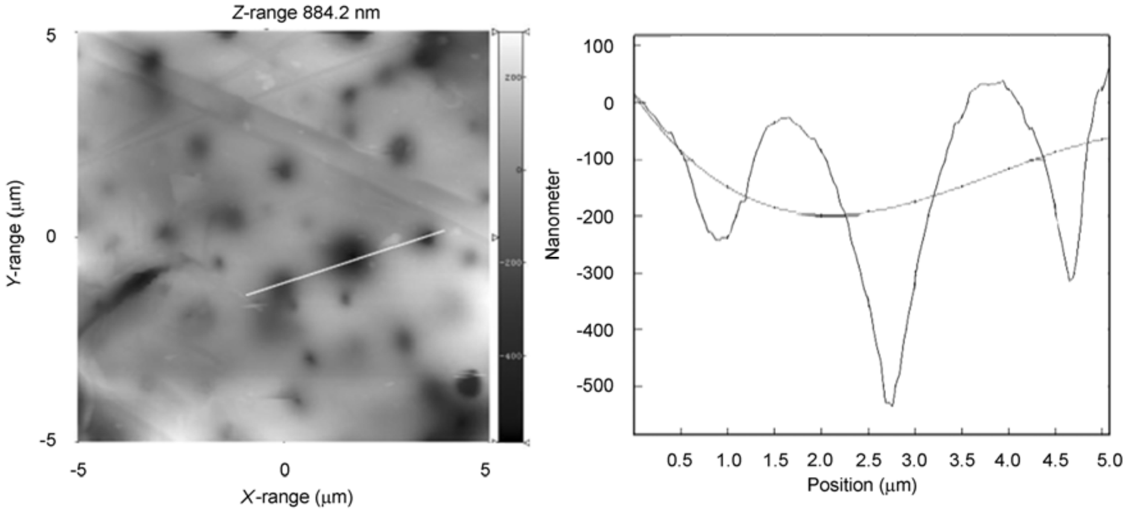

Fig.2 A top view and line profile of sample 1a.

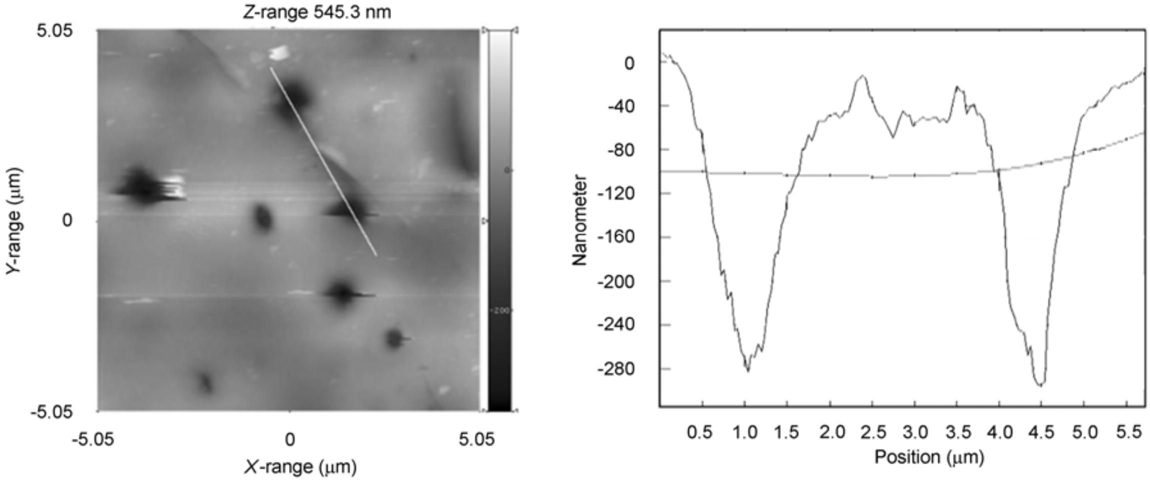

Fig.3 A top view and line profile of sample 1b.

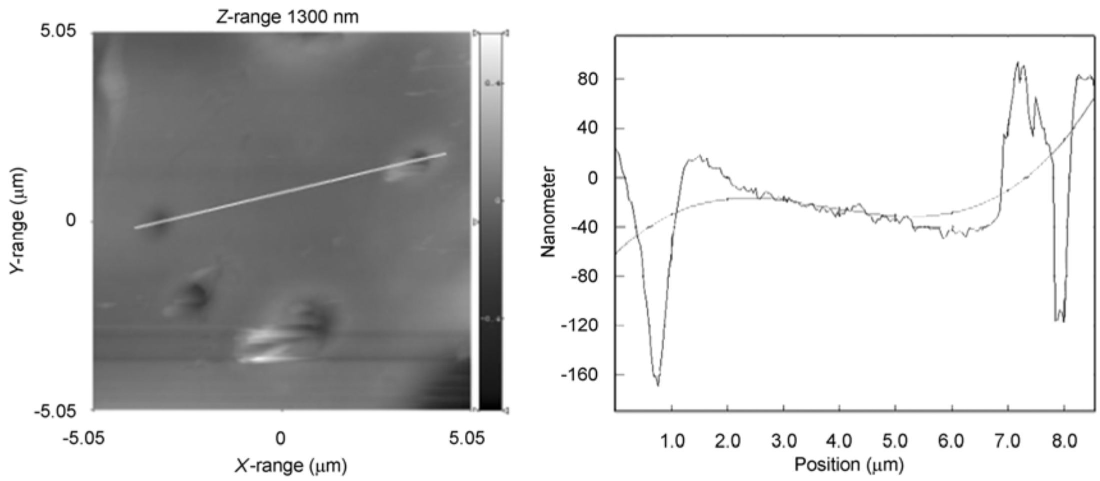

Fig.4 A top view and line profile of sample 1d.

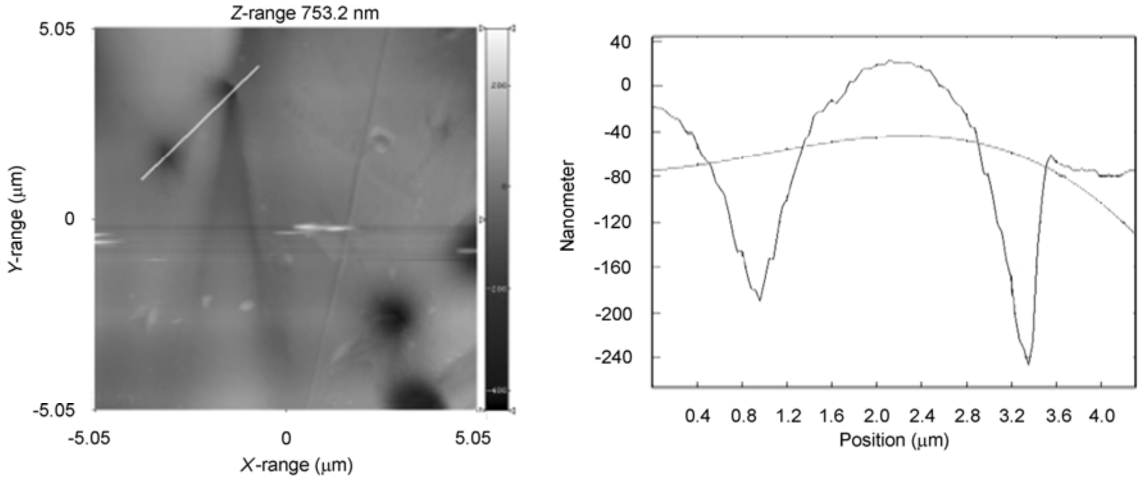

Fig.5 A top views and line profiles of samples 1e.

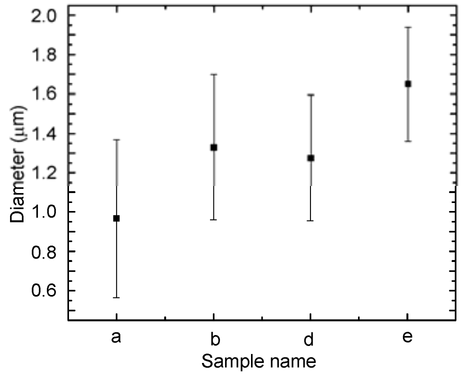

Fig.6 The diameter of different samples.

The results of 1d-sample are shown in Fig.4. There were about 4-5 holes in 10μm×10μm area. The depth of the holes was about 160 nm. The average diameter of the holes was about 1.2 μm.

The results of the 1e-sample are shown in Fig.5. It was hard to obtain the image because the roughness of the surface of this sample was almost out of the range of AFM scan scales. A relatively flat area was however found from where the measurement was taken. There were 3-4 holes in 10μm×10μm area. The holes had different depths ranging from 200 nm to 240 nm. As shown in Fig.6, the average diameter of the holes on the surface was about 1.6μm. It appeared that the average diameter of the holes on different sample surfaces became larger with ascending evaporation time.

3.2 PALS measurements

In this study, o-Ps components of polymers with different sulfonation time and different evaporation time were measured at a constant temperature for which appropriate values of the material-dependent normalization parameter were unknown. In polymers, the values of τ_3 yielded a measure of the average size of the cavity, and I_3 reflected o-Ps formation probability. The values of free volume radius and the normalized free volume fraction parameter, calculated from Eqs.(1-3) are shown in Table 1 with different sulfonation time and in Table 2 with different evaporation time.

Table 1 The positron annihilation parameters at three different sulfonation times in SPEK-C films

Sulfonation time(h)	o-Ps lifetime τ_3 (ns)	Free volume radius R (Å)	Intensity I_3 (%)	Fractional free volume f_v/C (%)
1	1.3876±0.0161	2.2101	11.5828±0.2004	5.2377
2	1.4352±0.0123	2.2667	14.7718±0.1916	7.2062
3	1.3392±0.0160	2.1477	13.5060±0.2413	5.6045

Table 2 The positron annihilation parameters at different evaporation time

Sample (ascending time)	o-Ps lifetime τ_3 (ns)	Free volume radius R(Å)	Intensity I_3 (%)	f_v/C (%)
1a	1.3876±0.0161	2.2101	11.5828±0.2004	5.2377
1b	1.3855±0.0125	2.2081	11.1408±0.1488	5.0241
1c	1.3842±0.0093	2.2065	12.4600±0.1237	5.6068
1d	1.3514±0.0149	2.1635	12.7508±0.2126	5.4087
1e	1.3349±0.0134	2.1436	13.1243±0.2007	5.4150

3.3 Correlation of PALS and AFM

The longer sulfonation time was corresponding to the higher degree of sulfonation. The physical appearance could also change with the sulfonation degree of SPEK-C. This may be explained by the membrane formation process and the interaction between the solvent, non-solvent and polymers. In Table 1, the radius and intensity had a tendency to increase up to 2 h sulfonation time, but contracted at 3 h. Comparing Fig.1 with Fig.2, 3 h-image showed some ditches and no apparent hole on a rough surface, 1a-image seemed a less rough than that of 3 h-image and about 20 holes on the surface. If the sulfonation time is longer, there is more ion-exchange capacity and decreased area resistance. This can be explained in terms of molecular structure, benzene ring's loosely tightening and the packing of $-SO_3H$ chains.

Interestingly, the sample 1c showed a stronger change in surface roughness, and correspondingly, fractional free volume showed the maximum value in Table 2. After a sulfonic group was introduced into the benzene ring, the solubility of the sulfonated polymer in DMF increased because of its large phenolphthalein group in the chain. While the binary solutions were stirred to form casting solutions, more air bubbles were extracted according to evaporation time. Previously, polymer had good electrical resistance. As expected, the resistance and mechanical strength decreased. Hence, free volume radii decreased and intensities increased with ascending evaporation time. Furthermore, the layer became denser because of weak interaction between the solvent and SPEK-C polymer. Samples 1d and 1e showed lower fractional free volume in Table 2, less holes and relatively flat on the surfaces in Fig.4 and Fig.5.

4 Conclusion

Pore sizes and distribution determined from PALS and AFM measurements showed reasonable agreement. The comparison of the positron annihilation results and those obtained by AFM gives the opportunity to explain better the positron behavior in polymeric materials. By choice of the proper sulfonation degree and evaporation time, we can achieve excellent mechanical and electrochemical properties for different industrial requirements. With this knowledge, the objective is to continue a systemical investigation on the effect of sulfonation time and evaporation time of SPEK-C films.

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