Effect of Temperature and Pressure Treatment on the Porosity of Expanded Polytetrafluoroethylene Films

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ABSTRACT: Small-angle neutron scattering was performed on a series of expanded polytetrafluoroethylene membranes that were subjected to thermal treatment at a maximum of 320°C at pressures up to 517 kPa. The scattering data indicate the existence of monodisperse pores of 2.7-Å radius, and a polydisperse set of scatterers with surface fractal properties. The thermal treatment had no significant effect on the structure, given that the maximum temperature was below the softening point of the polymer. The effect of increasing pressure was to increase the fractal dimension and to decrease the porosity void fractions. A linear relationship was noted between the Porod invariant values and the applied pressure. The pressure treatment had no effect on the size of the 2.7-Å pores. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1579–1582, 2003

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INTRODUCTION

Expanded polytetrafluoroethylene (e-PTFE) is a material with a wide range of biomedical and other applications,[1] one of which is as porous media in electrochemical sensors.[2] Control of the diffusion of gases into electrochemical gas sensors is an important topic and this appears to be crucial to sensor response.[2] During the production of gas sensors, the e-PTFE membranes are subject to pressure when they are in contact with the electrode. In a recent publication, Hitchman et al.[3] concluded that "the electrolyte film next to the electrocatalyst site is the prime factor controlling the output," and, even more explicitly, "The manufacture of a porous electrode and its sintering to a porous membrane is largely empirical and not very reproducible." Part of the reason for these observations is that any changes in the e-PTFE porosity during the pressure treatment are poorly understood.

In general, accurate assessment of membrane porosity is difficult because all of the commonly used techniques have significant limitations, such as:

- Gas adsorption. Commonly used materials such as PTFE are poor gas adsorbents because of weak gas–substrate interactions. The low density of these materials further compounds this problem, given that most commercially available instruments do not have sufficient capacity for the relatively large sample sizes required for accurate surface area determination.
- Microscopic imaging techniques, such as SEM, are surface sensitive and provide no information concerning bulk porosity and its connectivity. There are also inherent problems with respect to quantifying this information.
- Intrusion techniques such as Hg porosimetry are not suitable for microporous materials because of the very high pressures required to access small pores, which can also significantly alter the porosity of soft materials such as PTFE.
- The high transmissions of thin-film PTFE to X-rays means that small-angle X-ray scattering is also not useful.

For these reasons, we have applied another, although generally less-accessible technique, small-angle neutron scattering (SANS), to the characterization of the porosity of these materials. In SANS the intensity of neutrons scattered as a function of scattering angle is measured. These data can be interpreted in terms of the total amount of porosity and the pore size distribution. The general equation for determining the differential scattering cross section, $d\Sigma/d\Omega$, from a polydisperse system is[4]

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$$\frac{d\Sigma}{d\Omega} = (\rho_s - \rho_p)^2 \int N_0 G(q,R)[V(R)]^2 f(R)dR \quad (1)$$

where q is the scattering wave vector defined by

$$q = \frac{4\pi}{\lambda}\sin(\theta) \qquad (2)$$

in which λ is the neutron wavelength and θ is one-half the scattering angle. In eq. (1), N_0 is the number density of the scattering particles, $G(q, R)$ is the scattering kernel, $V(R)$ is the particle volume, and $f(R)$ is the normalized size distribution function of the scattering particles (the porosity in the current case). The key parameter determining the scattering intensity (compared to its variation with q) is the term $(\rho_c - \rho_s)^2$, which is the difference in scattering length densities between the polymer and empty pore.

SANS also yields another parameter that is useful for the analysis of porous solids, the Porod invariant Q, defined by[5]

$$Q = \int_0^\infty I(q)q^2 \, dq \qquad (3)$$

which is related to the void fraction of the solid under investigation by[5]

$$Q = 2\pi(\rho_s - \rho_p)^2 \, \phi(1 - \phi) \qquad (4)$$

Values of Q based on the limited wave vector range of SANS instruments provide a useful comparison for variations in void fractions and surface areas.

SANS is also useful for the identification of fractal objects. For surface fractals Schmidt[6] and Kjems and Schofield[7] showed that

$$I(q) = I_0\Gamma(D - 1)\sin[\pi(D - 1)/2]_q^{-(6-D)}, \qquad (5)$$

where I_0 is a constant, $\Gamma(5 - D)$ is a gamma function, and D is the surface fractal dimension. Scattering from an object with globally smooth surfaces is characterized by a fractal dimension of $D = 2$, which results in classical Porod scattering proportional to q^{-4}.
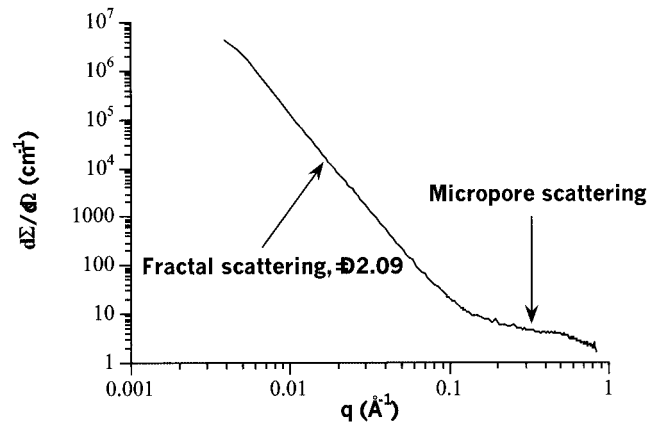

Figure 1   SANS for untreated e-PTFE.

In this study we present and analyze SANS results for a series of e-PTFE membranes that have been subjected to temperature and pressure regimes to assess their effects on porosity. In addition the effects of mild thermal treatment, below the softening point of the PTFE, were also monitored.

EXPERIMENTAL

Samples of e-PTFE were obtained from Gore, plc. (Livingston, Scotland). The film thickness of the samples was 0.33 mm. The thermal and pressure treatments imposed on these samples are presented in Table I.

SANS was performed at the ILL neutron source in Grenoble, France. This is a reactor neutron source, which produces cold neutrons by the use of a liquid deuterium moderator at 25 K. Instrument D22 was used because of the high q range offered by this instrument, and a neutron wavelength of 4.54 Å was chosen. The PTFE disks were attached to cadmium masks, and scattering was performed for 1 h at three detector distances to span the range, $0.004 < q(\text{Å}^{-1}) < 0.83$. The data were corrected with respect to background and empty cell scattering, such that $I(q)$ is presented in terms of the absolute differential scattering cross section ($d\Sigma/d\Omega$).

RESULTS AND DISCUSSION

The neutron transmissions of all the e-PTFE samples were on the order of 90%, which suggests that multiple scattering did not affect the results.

Figure 1 shows the scattering data for the untreated e-PTFE sample. As shown, there are two distinct scattering regions. In the range $0.004 < q(\text{Å}^{-1}) < 0.08$, the scattering intensity increases linearly on a log–log plot with decreasing q, indicating a power law dependency. This behavior is characteristic of fractal scattering. The slope of the curve is -3.90, which, according to eq. (5), corresponds to a fractal dimension of 2.10.
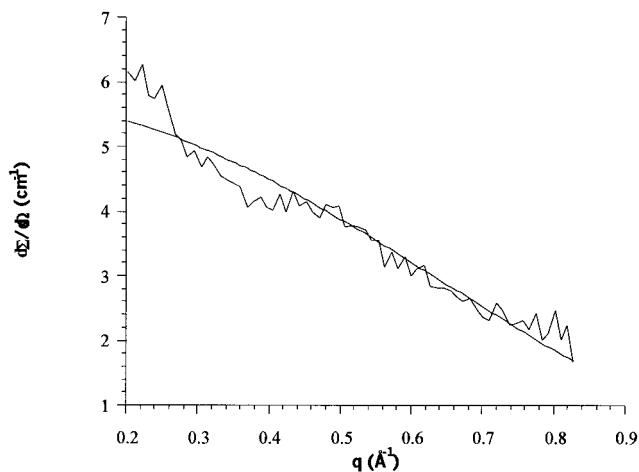
TABLE I
Thermal and Pressure Pretreatments

Sample	Pressure (kPa)	Heat treatment (°C)
1	None	None
2	None	270
3	None	290
4	None	300
5	None	310
6	None	320
7	276	300
8	414	300
9	517	300

Figure 2 Guinier plot for SANS on e-PTFE.

There are severe sensitivity issues over the calculation of fractal dimensions, given that changing the q range over which the determination is made by even slight amounts can have large effects on the calculated fractal dimensions. The method described by Hall et al.[8] was used to overcome these difficulties. To compare the fractal dimensions of the thermally and pressure-treated samples, the range $0.007 > q(\text{Å}^{-1}) < 0.08$ was used. In all cases the regression coefficient of the linear fit was 0.995, and the resultant estimated error in the value of the fractal dimensions was ±0.03.

The fractal dimension of 2.10 for the untreated e-PTFE represents a statistically significant deviation from classical Porod scattering, and the presence of some global surface roughness. However, it does not compare to the surface roughness encountered in some of the highly convoluted surfaces encountered in active carbons, for example, where fractal dimensions can approach values of 3.[9] The smooth nature of the surfaces in e-PTFE was previously established with SEM and other imaging techniques.[1] However, the SANS technique is sensitive to structure at much smaller length scales, and has the advantage over imaging techniques that any surface roughness can be easily detected and quantified. The upward deviation from the fractal scattering curve at high q was observed for a wide variety of materials including carbons and polymers.[10,11] It is caused by scattering from micropores in the e-PTFE and, based on previous work, the shape is characteristic of scattering from objects with a narrow size distribution. Therefore, instead of applying the general scattering equation for polydisperse systems , it is worth examining a simpler, that is, the Guinier equation for scattering from monodisperse spherical objects[12]:

$$I(q) = I(o) \exp \left(\frac{-q^2 R_g^2}{3} \right) \qquad (6)$$

where R_g is the radius of gyration. When the Guinier law is followed, a plot of $\ln[I(q)]$ versus q^2 results, and R_g can be determined from the slope of the curve. For spheres, the radius of the scattering object R is related to R_g by

$$R_g^2 = \frac{3}{5} R^2 \qquad (7)$$

Figure 2 presents the Guinier plot of the data presented in Figure 1, for $q > 0.1 \text{ Å}^{-1}$. As shown, it exhibits a linear form, and from the resultant slope, scattering in this region can be attributed to monodisperse spherical scatterers (i.e., pores) of 2.7 Å. The slight upward deviation of the Guinier plot at low q values suggests the presence of some polydispersity in scatterer sizes. This is consistent with the fractal nature of the scattering at low q, given that fractal objects are associated with power law size distributions of scattering object sizes.

The effect of varying heat treatment on the porosity of the e-PTFE samples is presented in Figure 3. As shown, the thermal treatment has no effect on the porosity of the PTFE, and is a good illustration of the reproducibility of the technique. This is what would be expected, given that the thermal treatments were all below the melting or softening points for this polymer, which DSC analysis has shown to occur at 322°C.

Figure 4 presents the effects of different pressure regimes on the porosity of the PTFE films. Scattering in the micropore region at high q remains unaltered, suggesting that the 2.7-Å radius scattering objects, identified in the untreated sample, remain unchanged. However, there are large changes in the low q region that correspond to scattering from meso- and macroporosity. There are actually two major changes in this scattering region: (1) a decrease in the slope of the line and (2) a reduction in scattering intensity with increasing pressure.
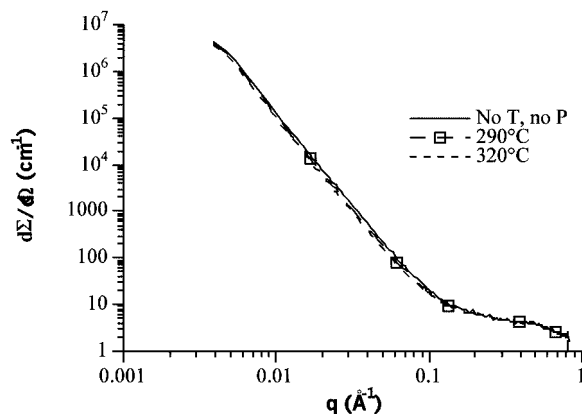

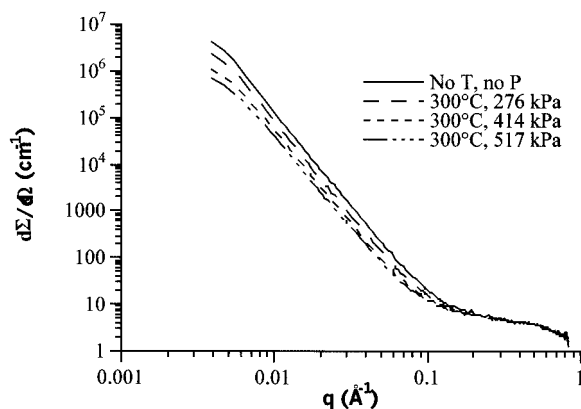**Figure 3** Effect of thermal treatment alone on SANS on e-PTFE.

Figure 4   Effect of pressure treatment on SANS on e-PTFE.

Figure 5   Correlation between applied pressure and PI values derived from SANS on e-PTFE.

The resultant fractal dimensions of the scattering curves in the linear fractal region are presented in Table II. The untreated and 276-kPa treated samples exhibit similar fractal dimensions. The 414-kPa sample shows a statistically significant increase in fractal dimension over that of these other two samples. The 517-kPa treated sample exhibits a larger increase in fractal dimension, attributable to an even rougher surface. Changes in fractal dimension have been related to changes in permeability and diffusivity, but it is unclear whether the changes observed here are sufficiently large to significantly alter these characteristics for the e-PTFE films.

The variations in scattering intensities can be quantified by the corresponding Porod invariants Q from eq. (3). The corresponding values are also presented in Table II. Figure 5 shows the relationship between the Q values and the applied pressure. This confirms that increasing the treatment pressure decreases the void fraction of the PTFE films in the region of larger porosity in an almost linear fashion. This implies that it is possible to control the film porosity, at least for the larger pores, by controlling the amount of applied pressure.

CONCLUSIONS

It has been demonstrated that SANS is a very useful technique for analysis of the porosity of e-PTFE films.

TABLE II
Fractal Dimension and Porod Invariant (PI) Values for the Pressure-Treated Samples

Sample	Fractal dimension	PI (arbitrary units)
1	2.09	0.93
7	2.10	0.78
8	2.16	0.70
9	2.24	0.67

The data indicate the existence of micropores with a narrow size distribution of mean radius 2.7 Å, and a polydisperse distribution of larger pores characterized by a fractal dimension of 2.09, which represents a globally smooth surface. It has also been shown that thermal treatments below the softening and melting points had no affect on the resultant pore structure. The effect of pressure treatments of up to 517 kPa was to increase the surface roughness and to decrease the overall void fraction. The size and amount of the 2.7-Å radius micropores remained unchanged by this treatment. This could have important implications for the preparation of sensor membranes.

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