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Investigation of mechanical damage in PFSA membrane via gas permeation rate test of membrane blister

Xiangyang Zhou[1,*], Diankai Qiu[1,*], Linfa Peng[1] and Xinmin Lai[1,2]

[1]State Key Laboratory of Mechanical System and Vibration, Shanghai Jiao Tong University

[2]Shanghai Key Laboratory of Digital Manufacture for Thin-walled Structures,

Shanghai Jiao Tong University Shanghai, China

e-mail: zhouxiangyang@sjtu.edu.cn

Abstract. The perfluorinated sulfonic-acid (PFSA) membrane is a key component in proton exchange membrane (PEM) fuel cells. The gas permeability of PFSA membrane, related to its deformation and damage, affects the performance and safety of the fuel cell. On the basis of constitutive model and solution-diffusion model of PFSA membrane, a numerical model was built to predict the deformation and gas permeation rate of membrane blister. The result indicates that damage occurs during the blister and accelerate the gas permeation.

Keywords: component; proton exchange membrane; numerical model; constitutive model; gas permeation; blister

1. Introduction

Mechanical damage in polymers is a multiscale process. In past few decades, researchers have extensively explored the fatigue and fracture property of polymers at macro scale [1]. While at micro scale, researches on damage in polymers are limited due to difficulties in observation of damage. As for some functional polymetric membranes, however, the accumulating microscopic damage might have resulted in the degradation of its function before its macroscopic fracture. For example, perfluorinated sulfonic-acid (PFSA) ionomer, with its remarkable ion-conductivity, is widely used as the proton exchange membrane (PEM) in PEM fuel cells [2]. It also separates reactant gases at anode and cathode. Exposed to fuel cell environment, however, the membrane degrades gradually due to mechanical stress [3], resulting in the increasement of transmembrane permeation of reactant gases. The transmembrane permeation of hydrogen inevitably brings about power loss and potential safety hazard [4]. Thus, it is of vital significance to investigate the effect of damage on gas permeability of polymeric membranes.

According to solution-diffusion model, the gas molecules permeate from high-pressure side to another due to difference of gas concentration. The permeation rate $J_i(\mathrm{mol/s})$ in discrete form can be given by [5]:

$$J_i =-\sum_{j=1}^{n} P_i \frac{\triangle p}{\delta_j} \Delta A_j \qquad (1)$$

where Pi is gas permeability coefficient of gas i, $\triangle p$ is pressure difference, ΔA_j and δ_j are element area of the specimen and its thickness respectively. According to (1), higher pressure and thinner membrane leads to more severe gas permeation. Besides, the gas permeability, related to the microstructure of the material, might also change due to mechanical damage[6], providing a new possible way to investigate the microscopic damage in polymers.

In PEM fuel cells, the PFSA membrane is exposed to complicated loading conditions, including multiaxial stress due to assembly, cyclic loading due to varied temperature and humidity and impulsive loading due to gas injection [3]. Blister test is a typical biaxial loading test and is used to test the mechanical property of PFSA membrane in previous works. Grohs el al. [7] tested the burst strength of PFSA membrane by blister test at different temperatures. Pestrak et al. [8] tested the biaxial fatigue life of PFSA membrane by blister test and roughly estimated the gas permeation according to pressure loss. It can be seen that the blister test is an effective and widely used experimental method of PFSA membrane. In this work, the gas permeation was accurately measured through a gas flow meter.

During the blister test, the increasing area and decreasing thickness of PFSA membrane all accelerates gas transmembrane permeation according to (1). To obtain the deformation data of membrane blister, a numerical model of membrane blister is built in Abaqus. The constitutive model of PFSA membrane was built by Silberstein et al. [9] and was implemented through a VUMAT subroutine in this work. The numerical model shows great accuracy in prediction of blister shape. On the basis of the numerical model, the uneven deformation data was obtained and applied in the calculation of gas permeation. The result shows that the numerical model is able to predict the gas permeation rate during blister test of PFSA membrane, with the deviation less than 7%. The result also indicates that damage might occur and accelerate gas permeation.

2. Experiment and numerical model

2.1 Experiment

As shown in Fig.1, a testing system of membrane blister test was built, which was composed of gas reservoir, relief valve, flow meter and blister apparatus. The blister apparatus is further composed of top plate and bottom plate. The membrane was clamped between the top and bottom plate, and a sealing gasket is assembled in the sealing groove on the bottom plate, insuring the airtightness of the apparatus. Before the blister test, the commercially available PFSA membrane NafionTM 211 (with the thickness of 25.4 μm) was dried in a vacuum oven at room temperature for 2 hours, and then cut into rounded sample and assembled in the blister apparatus. During the blister test, the hole in bottom plate was filled with high-pressure gas (helium and nitrogen) when opening the gas reservoir, of which pressure value was controlled by a relief valve. The testing pressure (difference between absolute pressure at high-pressure side and atmospheric pressure at low-pressure side) was set as 8.7 kPa, 18.7 kPa and 28.7 kPa. The testing pressures are so low that the membrane will not burst in 4 hours, so that the permeation rate can be measured.

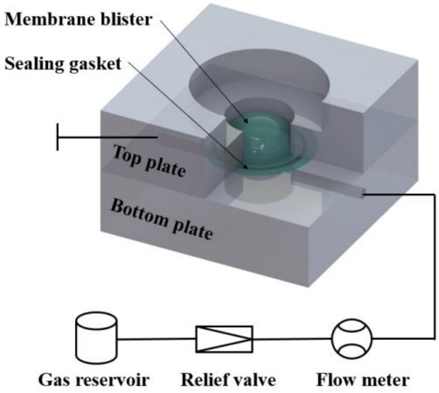

Fig. 1 An image of testing system in progress.

The whole testing process lasted 1 hour for each sample. In the first 45 minutes the flow meter (Alicat M series) was closed waiting for the stabilization of the membrane blister. And in the last 15 minutes, the flow meter was opened and the gas permeation through the membrane blister was measured. Fig.2 depicts the raw pressure and helium permeation rate versus time data in the last 15 minutes. Due to the operating principle of differential gas flowmeter, the pressure inside the membrane blister will drop slightly and finally stabilize over time. As shown in Fig.2 (a), the absolute pressure drops from 8.7 kPa to 8.2 kPa in 15 min, while drops from 28.7 kPa to 27.2 kPa in 15 min. As shown in Fig.2 (b), the helium permeation rate increases and stabilized to a certain value in 15 min. During the blister test, besides, the height of the membrane blister can be directly measured and was regarded as the characterization of the blister shape. The environment temperature and humidity was 25±2℃ and 50±5%RH respectively. And all the tests are repeated 3 times to obtain credible results.

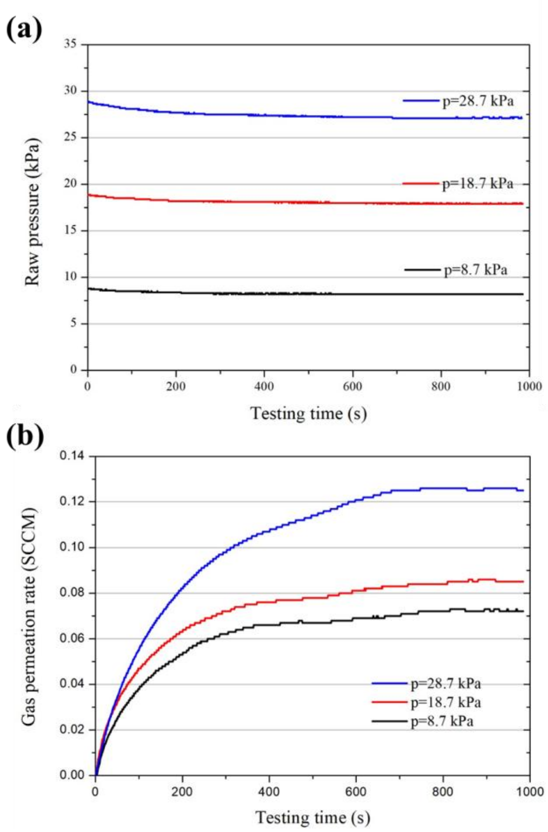

Fig. 2 (a) Raw pressure versus time data; (b) raw helium permeation rate versus time data.

It should be noting that the tested gas permeation rate includes two parts:

$$Q_{\text{test},i} = Q_{\text{permeation},\,i} + Q_{\text{blister}} \qquad (2)$$

where $Q_{\text{permeation},i}$ denotes the real gas transmembrane permeation of gas i, and Q_{blister} denotes the volumetric flow rate caused by the increasement of the volume of membrane blister. To eliminate the influence of Q_{blister}, another testing gas, nitrogen, was also applied. The gas permeability of nitrogen is so low (less than 1% compared with helium [6]) that the tested nitrogen permeation rate is equal to Q_{blister} in (2). As a consequence, the real helium permeation rate $Q_{\text{permeation},\,h\text{elium}}$ is given by:

$$Q_{\text{permeation},h\text{elium}} = Q_{\text{test},h\text{elium}} - Q_{\text{test,niteogen}} \qquad (3)$$

The tested permeation rate of nitrogen is quite low (about 5% compared with helium), which indicates that the membrane blister is relatively stable.

2.2 Numerical model

All simulations are run in ABAQUS/Dynamic. Fig. 3 (a) shows the constitutive model of PFSA membrane [9], of which model equations and parameters are listed in Table1. and Table 2. Fig.3 (b) shows the displacement nephogram of membrane blister at testing pressure of 28.7 kPa for 1 hour. The geometry of the part in simulation is the same with the real sample, with the blister diameter of 30 mm and thickness of 25.4 μ m. The circular edge of the part is fixed due to the clamping of the apparatus. Normal pressure is applied at down side of the part so that the blister forms. The value of normal pressure also keeps the same with real testing pressure.

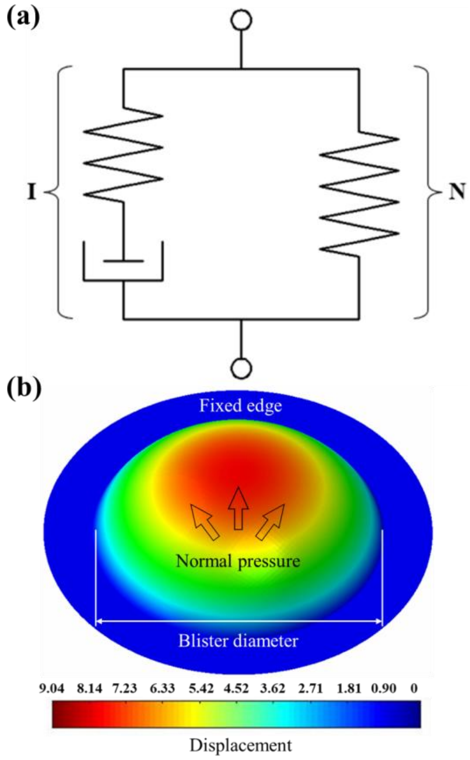

Fig. 3 (a) Constitutive model of PFSA membrane; (b) displacement nephogram of membrane blister in numerical model at testing pressure of 28.7 kPa for 1 hour and its loading setting.

Table 1. Summary of equations of the constitutive model

Items	Equations
Kinematics	$F = F^eF^p, b = FF^T, \bar{b} = J^{-2/3}b,\ J = \det(F)$ (4) $b^e = F^eF^{e,T}, \bar{b}^e = J^{e-2/3}b^e,\ J^e = \det(F^e)$ (5)
Stress	$\sigma_I = \frac{\mu_I}{J^e}dev(\bar{b}^e) + \kappa(J^e - 1)I$ (6) $\sigma_N = \frac{\mu_N}{J}dev(\bar{b}) + \kappa(J - 1)I$ (7) $\sigma = \sigma_I + \sigma_N$ (8)
Flow rule	$\bar{D}^p = \dot{\gamma}^p N, N = \frac{dev(\sigma_I)}{\|dev(\sigma_I)\|_F}$ (9)
Isotropic hardening	$\dot{\gamma}^p = \gamma_0 \exp\left(-\frac{\Delta G}{k_b\theta}\right)\sinh\left(\frac{\Delta G}{k_b\theta}\frac{\|dev(\sigma_I)\|_F}{(r_y + r_i)\hat{\tau}}\right)$ (10) $\dot{r_y} = h\left(1 - \frac{r_y}{r_{max}}\right)\dot{\gamma}^p, r_i = g\left(\sqrt{\frac{tr(b)}{3}} - 1\right)$ (11)

Table 2.Summary of constitutive model parameters

Items	Value	Items	Value	Items	Value
μ_I	110 MPa	$\Delta G/k_b$	6504 K	r_{y0}	1
μ_N	3.3 MPa	h	10MPa	r_{max}	1.48
κ	330 MPa	g	3.8 MPa		
$\dot{\gamma}_0$	6.72 s^{-1}	$\hat{\tau}$	9.2		

3. Result and discussion

3.1 Analysis of membrane blister

To validate the correctness of the numerical model, the height of membrane blister was measured and compared with the simulation results. As shown in Fig.4 (a), with the increasement of testing pressure, the height of membrane blister increases almost linearly. The height is only 4.08 mm at testing pressure of 8.7 kPa, while reaches to 9.04 mm at testing pressure of 28.7 kPa. And the numerical model shows great accuracy in predicting the height of membrane blister. On the basis of the numerical model, the full-scale shape and unevenly distributed thickness of membrane blister can be obtained, as shown in Fig.4 (b).

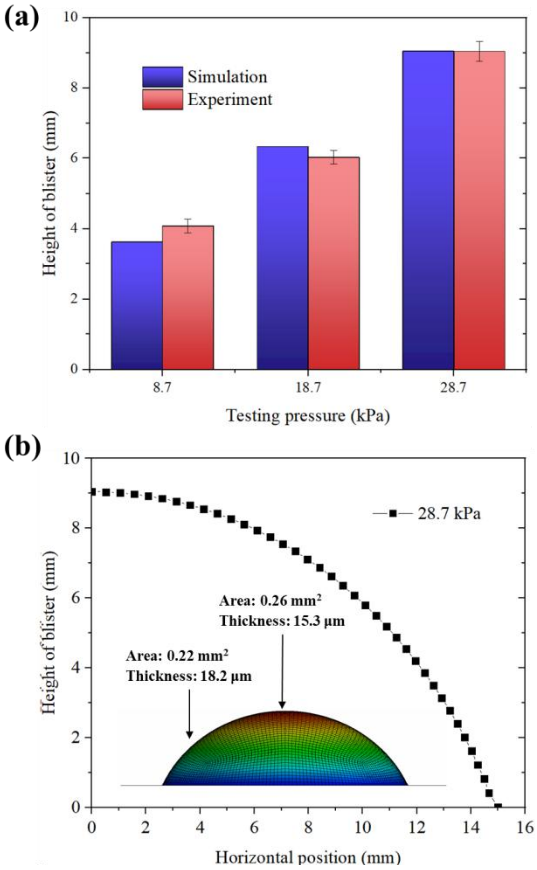

Fig. 4 (a) Comparison of height of membrane blister between simulation and experiment at different testing pressures; (b) cross-section profile of membrane blister at testing pressure of 28.7 kPa and process of data extraction.

3.2 Prediction of gas permeation and damage analysis

Based on the obtained data from numerical model, the gas permeation of membrane blister can be calculated according to (1) and compared with experiment result measured by gas flow meter. As shown in Fig.5, the helium permeation rate through PFSA membrane increases with testing pressure due to growing area and decreasing membrane thickness. The helium permeation rate through the PFSA membrane blister is 0.074 SCCM at testing pressure of 8.7 kPa, while reaches to 0.095 SCCM and 0.149 SCCM at testing pressure of 18.7 kPa and 28.7 kPa. And the numerical model is capable to predict the gas permeation rate of PFSA membrane blister, with the error less than 7%. It can also be seen that the deviation between experiment and numerical model gets larger with the increasement of testing pressure. One possible reason is that mechanical damage occurs during the blister test and the gas permeability coefficient increases, which further accelerates the gas permeation through the membrane.

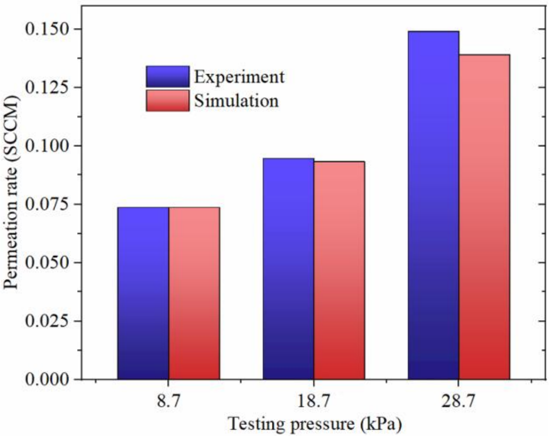

Fig. 5 Comparison of helium permeation rate between simulation and experiment.

The PFSA membrane separates reactant gases at anode and cathode in PEM fuel cells. The transmembrane permeation of reactant gases results in power loss and safety hazard. According to solution-diffusion model, the gas permeation rate through the membrane is closely related to its area and thickness. Thus, the varied shape of the membrane changes the gas permeation rate. As a widely used experimental method of biaxial loading, the blister test is also used to investigate the influence of deformation on gas permeation in this work. An apparatus of membrane blister test was built, where the membrane was exposed to normal pressure for 1 hour to form the blister and the gas permeation rate was also measured.

On the basis of constitutive model and solution-diffusion model of PFSA membrane, this paper establishes a numerical model of membrane blister and predicts its shape and gas permeation rate. The numerical model shows great accuracy in predicting the height of membrane blister. Based on the numerical model, the full-scale shape and unevenly distributed thickness of membrane blister can be obtained and applied in calculation of gas permeation rate. The result shows that the present model is capable to predict the gas permeation rate of membrane blister, with the error less than 7%. Besides, the increasing error with testing pressure indicates that damage might occurs during the blister test and accelerate the gas permeation.

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