



Effect of water on life prediction of liquid silicone rubber seals in polymer electrolyte membrane fuel cell

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ABSTRACT

Liquid silicone rubber (LSR) is a popular gasket or seal material and is also promising for sealing applications in polymer electrolyte membrane fuel cell (PEMFC). The durability of the LSR gasket/seals in PEMFC is one of the major issues in commercialization of PEMFC. As there are water and humidity inside PEMFC and polymers such as LSR generally exhibit stress relaxation property, it is important to understand the effect of water on the compression stress relaxation of LSR. Our test results show that water has no influence on the stress relaxation in the beginning, but it accelerates the relaxation after a certain time. Higher temperature makes this transition occurs earlier. Further studies reveal that water can diffuse into LSR and exists as free water molecules. It may attack the backbones of the polymer and thus accelerate the stress relaxation. High temperature tends to aggravate the attack of water to the polymer chains. The attack coexists with the thermal degradation of the LSR.

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) converts hydrogen fuel into an electric current directly. It has great potential as a power source for automobile and other portable or stationary devices due to the relatively low operation temperature and high efficiency. To commercialize PEMFC and to have wide application of PEMFC, there are several durability issues that need to be resolved. Among those issues, the long term stability and durability of gaskets/seals are critical, yet overlooked oftentimes.

The sealing function of gaskets in PEMFC is to hold the gas and liquid inside the fuel channels from leaking or escaping. Gasket is usually made of polymeric material due to its low cost, flexibility, and chemical and physical stability. However, gasket may degrade with the operation of a PEMFC as it is exposed to acid, humidity as well as temperature cycles. Husar et al. [1] reported gasket failure in PEM fuel cell stack testing. Tian et al. [2] detailed compartment leak in a PEMFC resulting from gasket failure. Some researchers have investigated the effect of temperature and simulated PEMFC solution on several gasket candidate materials. Tan et al. [3–9] studied the chemical and mechanical degradation of candidate gasket materials in either a simulated PEMFC or an accelerated test environment. Several gasket materials such as liquid silicone rubber (LSR) were first aged in simulated PEMFC environments at various temperatures. Chemical and mechanical

properties of these aged materials were then examined using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Dynamic Mechanical Analyzer (DMA) and other techniques. Results show that the surface chemistry of the aged samples changed and some chemicals leached out into the solution. However, interestingly, the bulk mechanical properties of the sample, such as storage modulus and loss modulus, remain unchanged [10].

Ghanbari-Slahkali et al. [11] studied the change of surface chemistry of LSR aged in de-ionized (DI) water for 2 years. After a series of characterization with various techniques, they reported that the hydrothermal degradation of the sample is only limited to 100 μm deep from the surface. Meanwhile, a significant weight reduction was observed. They also proposed a plausible reaction mechanism which shows how water attacks the backbone of the silicone rubber. Other work in the area of biomedical field also shades some light to the degradation of medical grade polymeric materials at elevated temperatures [12,13].

In sealing applications, gasket or seal is compressed to bear a certain load or pressure. The level of the compressive stress or pressure at the seal directly dictates the sealing ability. However, most of the work discussed above focused on studying the mechanical or chemical degradation of the seal materials. However, the loss of the sealing ability of polymeric gasket or seals is not only due to the surface chemistry or hardness change, but also the 'stress relaxation' property.

Polymeric materials are known to be viscoelastic and the stress and strain relationship strongly depends on time. The stress may decrease gradually with time when the strain is held constant,

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which is called ‘stress relaxation’. Under constant strain or deformation like in most sealing applications, the retained stress or force in the compressed seal gradually decreases with time and the material may eventually lose its sealing function. Though Tan et al. [4,5] aged the samples with an applied stress in their study of degradation of seal materials, it does not address the stress relaxation behavior of the polymeric samples in sealing applications.

Several factors may influence the compression stress relaxation of polymers, such as temperature, humidity, exposed solution and oxygen concentration and so on. Liu et al. [14] studied the stress relaxation of a Nafion® 117 membrane at 25% strain. Ronan et al. [15] used time–temperature superposition method to predict the long term stress relaxation behavior of elastomers. Bernstein and Gillen [16] predicted the lifetime of fluorosilicone o-rings with compression stress-relaxation measurements. Little work was on the influence of PEMFC solutions on the stress relaxation behavior of polymeric materials.

The work presented in this paper attempts to understand the stress relaxation behavior of polymeric gasket materials in PEMFC environment. Interestingly, our initial experiments show that the stress relaxations of LSR in PEMFC acid solution and DI water are nearly the same up to 1500 h (see Section 4). This conclusion was confirmed after several repeated tests. It is consistent with our previous studies that the bulk mechanical properties of polymeric gasket materials do not change as aged in PEMFC solutions [3–9], even the surface chemistry has changed somewhat. Because of this conclusion, our later studies were focused on the effect of water and temperature on the stress relaxation behavior of LSR material. It is assumed that the results can be applied to LSR in PEMFC environment.

2. Theory

More than hundred years ago, Svante Arrhenius developed a model to describe the chemical reaction rate. It states that the rate of chemical reaction is a function of absolute temperature. The original Arrhenius equation is as follows:

$$k = A e^{-Q/RT} \quad (1)$$

where k is any chemical reaction rate and Q is a special constant, called activation energy of the reaction. Activation energy is the energy barrier which has to be overcome for molecular motion to occur. A is a coefficient. R is the universal gas constant and T is the absolute temperature in Kelvin.

Because many failures or degradations result from chemical reactions, Arrhenius equation has been widely used for life estimation [17] of stress relaxation, creep, time to failure and others. For example, Ertel and Carstensen [18] adopted modified Arrhenius relationship to predict pharmaceutical stability. Nelson and Labuza [19] used Arrhenius models to estimate shelf life in food engineering. Several countries even developed standards to predict the reliability of equipments using the Arrhenius equation [17]. As applied to stress relaxation, the Arrhenius equation can be written as:

$$\sigma = A(\varepsilon)te^{-Q/RT} \quad (2)$$

Eq. (2) can be re-written as:

$$\sigma = A(\varepsilon)te^{-Q/RT} = A(\varepsilon)\theta(t, T) \quad (3)$$

Therefore, at a critical time the following equation is valid:

$$\theta_c(t, T) = t_c e^{-Q/RT} \quad (4)$$

Rewrite the above equation in logarithmic form:

$$\log t_c = \frac{0.217Q}{T} + \log \theta_c(t, T) \quad (5)$$

According to Eq. (5), the activation energy Q can be obtained by plotting a straight line with the variables $1/T$ and $\log t_c$ [17]. The slope of the straight line is then $0.217Q$ [20]. Using this straight line generated by fitting with limited test data points, the service life t at any other temperature, typically lower, can then be estimated by an extrapolation. This is the basis for accelerated testing using the Arrhenius model.

3. Experiments

3.1. Materials and preparation

Liquid silicone rubber (LSR) is a commercially available high purity platinum-cured silicone rubber. It is a good candidate for gasket/seals in PEMFC because of its relatively low price and good performance. Its glass transition temperature at -40°C is relatively low and it remains flexible, elastic, and retains its properties up to 300°C . Like most polymers, LSR also shows viscoelastic behavior especially at high temperatures. In this paper, LSR in sheet form was obtained from a manufacturer and cut into round buttons for compression stress relaxation (CSR) tests.

Cylindrical disc with a 13 mm diameter (D) and 6.3 mm height (H) was used in our experiments according to ASTM D6147 [21]. It is worth noting that it is not easy to make the samples perfectly cylindrical if it was directly punched out from a sheet material. A tool was designed and used to cut the sample out from the sheet to make it as cylindrical as possible.

A simulated PEMFC solution is used in this study. The composition of this solution is 12 ppm H_2SO_4 , 1.8 ppm HF with reagent grade water having 18 M Ω resistance. The solution's pH value is 3.35, which is close to that experienced in real PEM fuel cell which ranges from 3 to 4 [8].

3.2. Instrument

The stress relaxation tests were done using Elastocon AB, Sweden equipment. This instrument consists of three independent rigs. Each rig has a load cell and a container that can test a sample at a certain temperature and submerged in liquid – see Ref. [22] for details about the relaxation rigs.

Generally, there are two types of stress relaxation test – one is continuous (method A) and the other is intermittent (method B) as outlined in ASTM D6147 [21]. In method A, the force is recorded continuously throughout the test at the test temperature. On the other hand, in method B, the sample is taken out of the test environment from time to time, and the force is measured at room temperature. In this paper, method A, the continuous stress relaxation tests, is adopted, which is close to the practical application of gaskets or seals which is supposed to be under load constantly when in service.

Thermogravimetric analyzer (TGA) from TA instruments (Q500) was also used to measure the weight changes of LSR samples as a function of temperature in this study. The measurement is under N_2 environment at a flow rate of 15 ml min^{-1} . The sample was subjected to a constant heating rate ($10^\circ\text{C min}^{-1}$) from room temperature to about 500°C . Each sample weighs about 5 mg initially.

3.3. Tests

Compression stress relaxation tests were performed at 25°C , 70°C , 100°C , and 120°C . At each temperature, there were two tests: one in air and one in water. All the compression tests were

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