



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

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ARTICLE INFO

Article history:

Received 23 May 2011

Received in revised form 18 July 2011

Accepted 19 July 2011

Available online 26 July 2011

Keywords:

Water effect

Stress relaxation

Liquid silicone rubber

Polymer electrolyte membrane fuel cell

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 mechani-

cal 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 $18\text{M}\Omega$ 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 15ml 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

Table 1
Compression stress relaxation tests.

	Temperature (°C)	Strain level (%)	Initial load (N)
In ambient air	25	25	155
	70	25	163
	100	25	168
	120	25	170
In DI water	25	25	160
	70	25	173
	100	25	178
	120	25	176
In regular solution	70	25	170

performed with a 25% strain level. Table 1 is a summary of the tests. The wet condition was achieved by putting de-ionized water (DI water) in the container of the test rig so the specimen was completely immersed throughout the test. The container had a cover with seals and can keep the water vapor inside even at 100 °C and 120 °C (see [23] for the schematic of the container in the rig). Sufficient amounts of water were placed into the cell to ensure the sample has immersed at high temperature. This procedure is validated by the fact that the samples were still immersed in DI water after the test.

Note that ASTM D 6147 [21] requires the pre-conditioning of the test specimen and eliminating data from the first 30 min. However, this paper is to study the effect of water on the compression stress relaxation and not to generate standardized stress relaxation curves. Therefore, all data including those from the first 30 min and no pre-conditioning are used in the analysis thereafter.

4. Result and discussion

4.1. Effect of water and PEMFC solution on the stress relaxation of LSR

As noted in Section 1, this work attempts to understand the stress relaxation behavior of polymeric gasket materials in PEMFC environment. First we did stress relaxation tests in simulated fuel cell solution. In order to compare the effect of PH value on the stress relaxation of this material, we also did the same test but in DI water. As shown in Fig. 1, it turns out that the stress relaxation curves of LSR in acid solution and DI water are nearly the same up to 1500 h and it is confirmed after several repeated tests. It is somewhat consistent with our previous studies indicating that the bulk mechanical properties of polymeric gasket materials aged in PEMFC solutions did not change [3–9]. This result indicates that the different stress relaxation behaviors in ambient air and PEMFC environment is mainly due to the introduction of water. Because

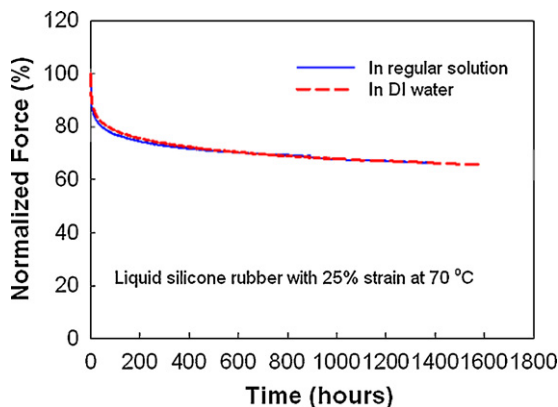


Fig. 1. The effect of regular solution and DI water on the stress relaxation of liquid silicone rubber.

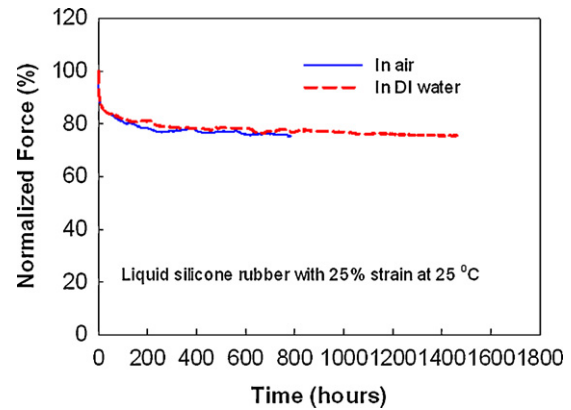


Fig. 2. Compression stress relaxation curves in air and DI water at 25 °C.

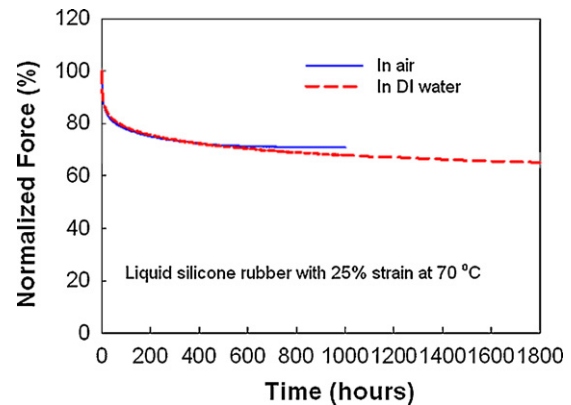


Fig. 3. Compression stress relaxation curves in air and DI water at 70 °C.

of this conclusion, we then studied the stress relaxation behavior of LSR material in water, which is easier to perform than in acidic PEMFC solution, in later tests. It is assumed that conclusions obtained for LSR in water can be applied to that in PEMFC environment.

4.2. Effect of water on compression stress relaxation of LSR

Figs. 2–5 show the comparison stress relaxation curves in air and water at 25 °C, 70 °C, 100 °C and 125 °C, respectively. It is noted that the data in Figs. 3–5 were obtained with the test samples inside the Elastocon oven, where the temperature is controlled very well, while the data in Fig. 2, on the other hand, were from tests

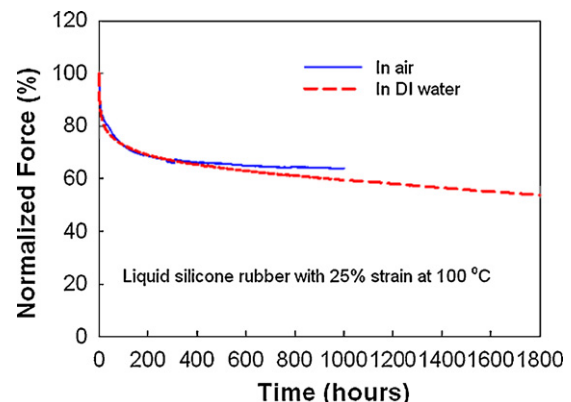


Fig. 4. Compression stress relaxation curves in air and DI water at 100 °C.

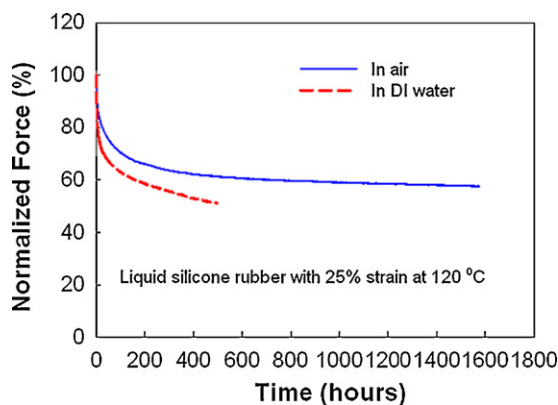


Fig. 5. Compression stress relaxation curves in air and DI water at 120 °C.

performed outside of the Elastocon oven using the same jig. The high frequency variation of the data shown in Fig. 2 is from the slight temperature variation in the laboratory room. It does not affect any conclusion from our work.

Comparing the two curves in each of Figs. 2–5, it can be seen that the two overlapped in the beginning and gradually deviated each other after some time. The stress relaxation in water obviously is faster, i.e. shown as the lower curve in Figs. 2–5. The specific time the two curves started to deviate each other heavily depends on the temperature, i.e. 800 h at 25 °C in Fig. 2, 600 h at 70 °C in Fig. 3, 400 h at 100 °C in Fig. 4 and near the beginning at 120 °C in Fig. 5.

Theoretically the stress a polymer can bear relies on the number of its network chains per unit volume provided the strain and temperature are constant. Continuous stress relaxation as in our tests reflects the chain scissions during the long term holding strain. The fact that the stress relaxes faster in DI water than in air indicates that polymer chains might be attacked by water and this attack can be accelerated by the increase of temperature. The mechanism on how water affects the stress relaxation is further investigated in Section 4.4.

4.3. Arrhenius plot

According to the Arrhenius model, e.g. Eq. (5), a plot displays the logarithm of the cutoff/failure time against the inverse of temperature can be used to predict the cutoff/failure time at another temperature. A straight line in the plot indicates a single rate-limited thermally activated process and the activation energy is proportional to the slope of the straight line.

Fig. 6 shows the Arrhenius plot corresponding to the stress relaxed to 76% of their initial values from Figs. 2–5. For the stress relaxation curves shown from Figs. 2–5, 76% is the minimum normalized stress that all the curves can reach, and that is how the cutoff 76% is chosen. The stress relaxation test at 25 °C ends with 76% normalized stress after more than thousand hours. It is shown that the Arrhenius plot is a nearly straight line for the test data in air, while a curvature is observed for that in DI water when the temperature is higher than about 100 °C.

According to the Arrhenius model, a constant slope would indicate the same activation energy and therefore the same mechanism for the reaction. The straight line shown in Fig. 6 for the data in air signifies the stress in the material relaxed with a single mechanism in temperature range 25–120 °C. This, however, is not true for the data from tests in water, which implies that a different stress relaxation mechanism might have occurred near 100 °C as the slope of the line starts to change as the temperature gets higher than 100 °C.

The phenomenon of curved Arrhenius plot is usually called non-Arrhenius behavior [24]. Celina et al. [25] reported the

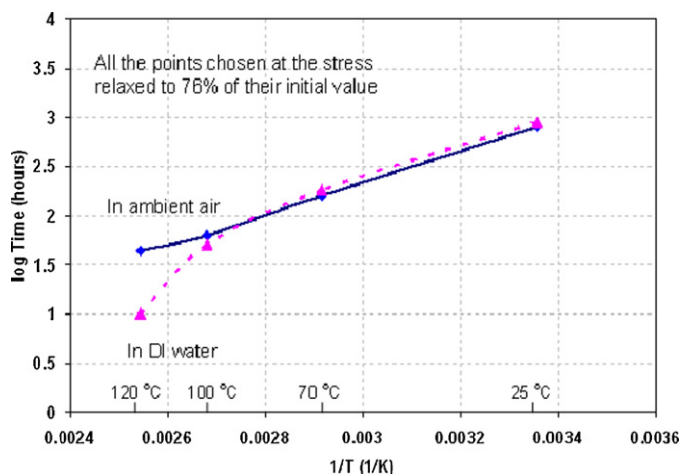


Fig. 6. Arrhenius plot for stress relaxation tests in air and water.

non-Arrhenius behavior in polymers, and they postulated that there were two competing processes, which have different activation energy resulting from different mechanisms. Consequently it induces a curvature for the Arrhenius plot. In other words, in one temperature region one process may dominate and in other region the other process may dominate.

In Fig. 6, 76% of the initial stress is selected as the cutoff stress to represent the failure or malfunction of the seal. Alternatively, if a lower cutoff value is chosen, say 65%, a similar Arrhenius plot would be obtained. The curve corresponding to 65% of the initial stress would be above the 76% curve and the curvature change would be shifted to lower temperature as shown in Fig. 7 schematically.

Arrhenius equation is widely used for accelerated service life or failure estimations. It is typical to predict the service life at lower temperature by using test data at higher temperature with shorter test time. The underlying assumption for life prediction using the Arrhenius model is that the reaction mechanism remains the same and activation energy does not change accordingly. For example, in Fig. 6, estimation of the service life in air at room temperature 25 °C using test data at higher temperature would be reasonable. However, for stress relaxation in DI water, the prediction for service life at room temperature using data at higher temperature would give erroneous, longer than real estimate.

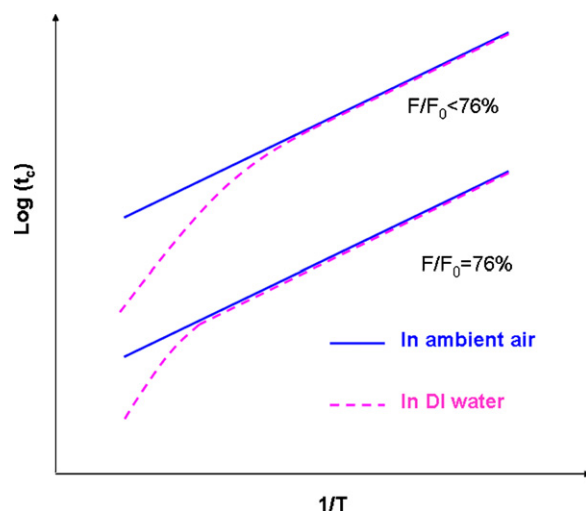


Fig. 7. Schematic of Arrhenius plot at two cut-off retaining forces – one at 76% and the other at <76% of the initial force.

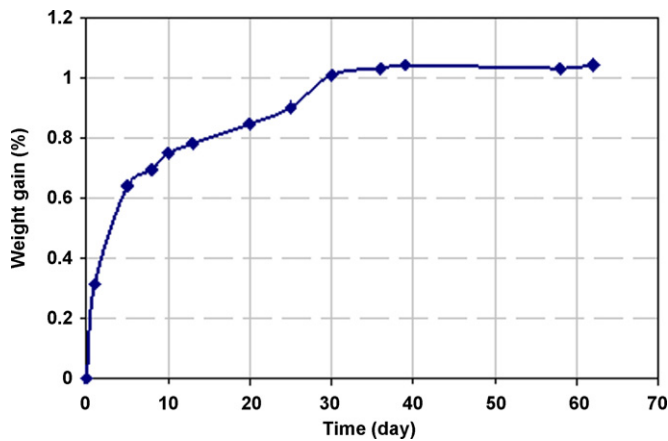


Fig. 8. Weight gain of LSR with time due to absorption of water at 70 °C.

4.4. Mechanisms

As discussed in previous sections, water accelerates the stress relaxation rate after a certain period of time and thus changes the reaction mechanisms, which is different from that of the relaxation without water. In this section, how the water affects the physical properties of the LSR is further investigated.

4.4.1. Water absorption

In order to study the effect of water on the LSR material, the water absorption test was performed. The percentage of water absorption in the sample is calculated by the weight change with the following equation:

$$\Delta m = \frac{m - m_0}{m_0} \times 100\% \quad (6)$$

where Δm is the percentage weight change, m is the weight of the exposed sample in DI water and m_0 is the initial weight of the sample.

Samples with a 13 mm diameter (D), 6.3 mm height (H), and an initial weight of 0.8600 g are used for the absorption tests. The sample is weighed before the test and then immersed in the DI water at 70 °C. The sample is taken out of the water at selected times and weighed with Sartorius Balance (model 1712 MP8 silver edition) after carefully removing the residue water on its surface. Fig. 8 shows the weight change as a function of time. It is shown that the weight increased sharply at the beginning and then gradually slowed down. After about 40 days, the value reaches a constant. The total/end water absorbed is about 1% of the sample's initial weight. This test data, as contrast to common belief, proves that LSR can absorb water, albeit small amount, especially in the beginning.

4.4.2. Swelling

Derham [23] reported that the absorption of liquid usually results in the swelling of the material, which would increase the stress when constrained. To study the potential influence of swelling on the relaxation stress of LSR, swelling tests were performed at 70 °C and 95 °C in this work. The samples were preheated to the test temperature. A small compression load about 1.5 N is applied to the sample and then immersed in the preheated water at 70 °C or 95 °C in a container. The entire test rigs are placed in the oven at 70 °C and 95 °C immediately and the computer starts to monitor the compressive stress variation simultaneously. The purpose of these tests is to study the influence of swelling, if any, on the change of stress in the sample under a constant mechanical strain. The preheating of the samples and the water are to ensure no

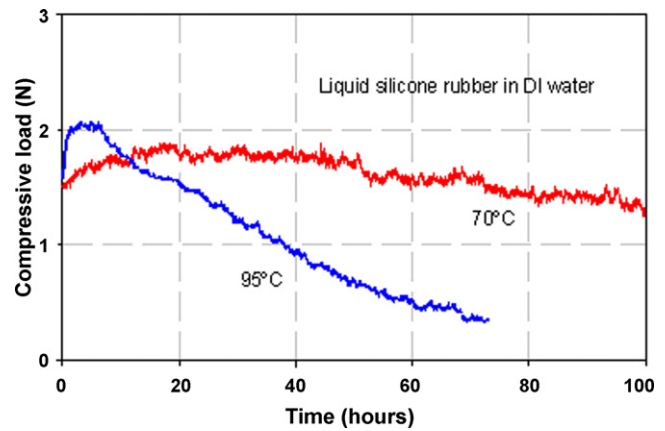


Fig. 9. The effect of swelling on the load variation.

influence from thermal expansion. Thus any change, i.e. increase, from the pre-load 1.5 N would be from the swelling of the sample.

Fig. 9 shows the test result. It is seen that the load increased slightly at the beginning. After that, the load starts to gradually decrease due to the relaxation of stress. Data in Fig. 9 demonstrates the little effect of swelling due to water absorption on the sample's stress change. This is consistent with the study of water absorption in Section 4.4.1 in which only a small amount of water is absorbed into LSR in the very beginning.

From the studies of water absorption (Fig. 8) and swelling (Fig. 9), it can be concluded that the difference in stress relaxation in between water and air observed in Figs. 2–5 is not due to swelling of the SLR samples.

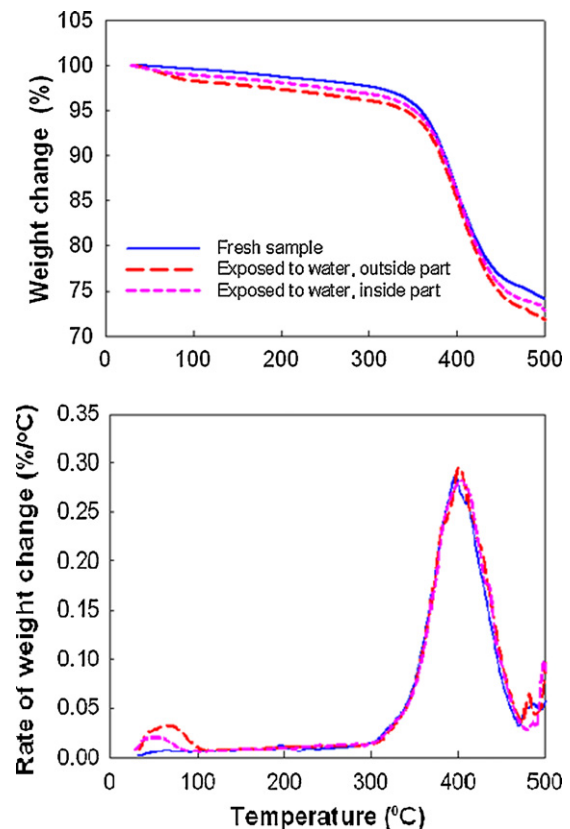


Fig. 10. TGA results showing: (a) weight change and (b) rate of weight change of LSR samples with temperature.

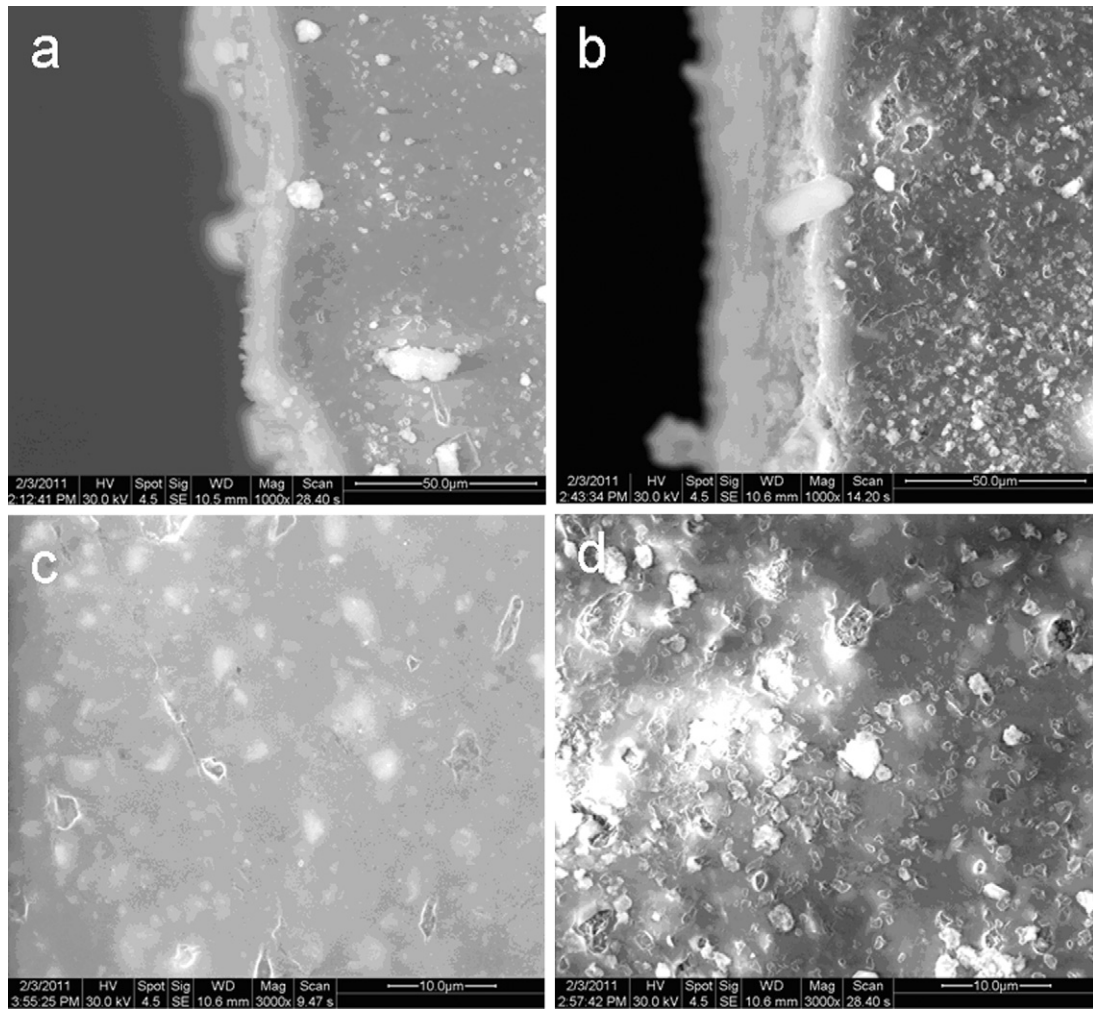


Fig. 11. Surface SEM images of LSR: (a) fresh sample at 1000 \times , (b) aged samples at 70 °C for three months at 1000 \times , (c) fresh sample at 3000 \times , and (d) aged sample at 70 °C for three months at 3000 \times ((a and b) are on the edge of the samples).

4.4.3. The state of the absorbed water

Water may be in different states when absorbed by polymers and the various state of water in a polymer could make the mechanical and physical properties of the polymer significantly different [26].

To study the state of water absorbed by our LSR sample, thermogravimetric analyzer (TGA) is used to measure the weight changes of the water-exposed sample with temperature. A LSR sample was exposed in DI water at 70° for four weeks. Two TGA specimens, weighted about 5 mg each, were cut from the surface and interior of the aged samples along with another fresh specimen.

In Fig. 10a, weight change curves show that water exposed samples lost weight more quickly than the fresh sample from the very beginning. And, the surface part of the sample losses weight quicker than the interior part, illustrating that the region of the sample near the surface contains more water than interior.

It is noted that the rate of the weight change shown in Fig. 10b indicates the water evaporated for each degree of temperature rise. As shown, there are peaks just before 100 °C for the exposed or aged samples, which signifies the higher degree of evaporation of water. The difference in height of the two peaks for the two exposed samples demonstrates that the exterior of the exposed sample had more water than the interior. After 100 °C, all three curves overlap very well. This indicates that water existed as free molecules when absorbed in liquid silicone rubber so they evaporated before/near 100 °C, the boiling point of water.

4.4.4. Scanning electron microscope

LSR samples aged in DI water at 70 °C for three months were used in this study. The surfaces of the aged samples are studied with scanning electron microscope (SEM). Fig. 11 shows the images of fresh and aged samples. It can be seen that the surface of aged samples are very rough compared with that of the fresh samples, which is very smooth. The little pores on the surface of the aged samples apparently are results from the attack of water on the polymer.

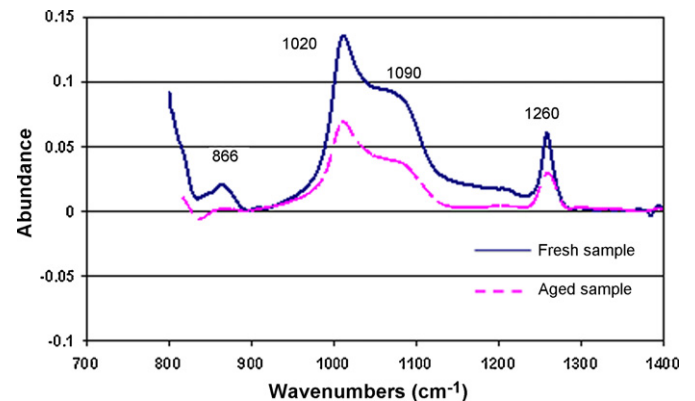


Fig. 12. Comparison of ART-FTIR spectra for fresh and aged LSR sample at 70 °C for 3 month.

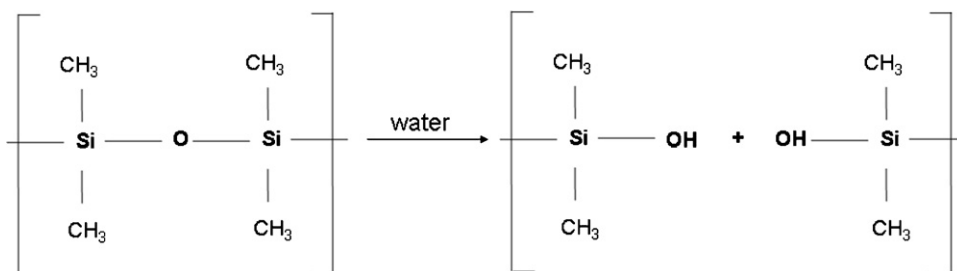


Fig. 13. Possible reaction mechanism of liquid silicone rubber with water [11].

4.4.5. ATR-FTIR

The ART-FTIR analysis can reveal the change of chemical bond after exposure to water at high temperature. Fig. 12 shows the comparison of the ART-FTIR spectra of the samples before and after aged in water for 3 month at 70 °C. The broad band between 1020 and 1090 cm^{-1} is from the vibration of ν (Si–O–Si) stretching mode. The intensities of the absorbance of the aged sample in this band are much lower than those of the fresh sample. In ATR-FTIR results for polymers, the intensity of the absorbance can reflect the chain length [27]. The decrease of the peaks shown in Fig. 12 may well be due to the chain scission of the backbone of the LSR caused by water attack. After the break of the backbone, the shorter chain may rotate and become disorder (and then reduce the intensity of the absorbance peaks). This can also explain why the peaks at 866 cm^{-1} and 1260 cm^{-1} , which are due to the ρ (Si–CH₃) rocking vibration and δ (Si–CH₃) bending mode, respectively, for the aged sample are also lower than those from the fresh sample.

4.4.6. Mechanism

Ghanbari-Slahkali et al. [11] studied the hydrothermal stability of cross-linked LSR at 100 °C in DI water for 2 years. They conclude that the degradation of LSR was only limited to about 100 μm layer from the surface and the material under this layer is intact. They proposed a reaction mechanism involving the attack of water to the Si–O–Si bond and the chain scission.

The mechanism proposed in [11] as shown in Fig. 13 can be used to explain our stress relaxation data. The diffused water attacks the Si–O–Si bond and decomposes the long chain into relative shorter ones. It is especially true in our tests, in which the samples bear load and at high temperatures. This mechanism is also supported by our leaching tests [9], which shows that several chemicals including silicone leached out into water when aged in water at high temperature. Note that this process is gradual and it takes time for water to diffuse into the polymer and then attack the backbone of the polymer. That is why water starts to accelerate the stress relaxation a few hundred of hours later rather than at the very beginning in Figs. 2–4. However, higher temperature apparently accelerates the diffusion of water into the polymer as well as its attack to the polymer backbone. When the temperature is high enough, such as 120 °C shown in Fig. 5, the effect of water on the stress relaxation appears to start from the beginning of the test.

5. Conclusion

This paper studies the effect of water on compression stress relaxation of liquid silicone rubber (LSR), a promising candidate gasket material for proton exchange membrane fuel cells (PEMFC). Experiments show that at lower temperature, water has no influence on the relaxation curves at the beginning. However, after a period of time, water starts to accelerate the relaxation rate. Increasing temperature makes the effect of water starting earlier.

Water can diffuse into liquid silicone rubber, though diffusion rate is slow. The water diffused into the polymer exists as free water molecules and they may attack the backbones of liquid silicone rubber and thus accelerate its stress relaxation. Temperature plays an important role in determining the attack rate and higher temperature tends to aggravate the attack to the backbones. The attack of water to polymer chains is an additional reaction with the thermal degradation in air.

Acknowledgements

This study is sponsored by NSF Industry/University Cooperative Research Center for Fuel Cells at the University of South Carolina and the US Department of Energy (DE-FC36-06G086041 and DE-FG36-08G088116) to the University of South Carolina Research Foundation. The material, liquid silicone rubber, was kindly provided by Dow-Corning Corporation (Dr. Peter Lo). Y.J. Chao also wants to thank the travel support from China 111 project (B08040) awarded to the School of Materials Science, Northwestern Polytechnical University, Xian, China.

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