



Service life estimation of liquid silicone rubber seals in polymer electrolyte membrane fuel cell environment

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ABSTRACT

Polymer electrolyte membrane fuel cell (PEMFC) is a promising power source for many applications such as automobiles. Sealing around the perimeter of the cell is required to prevent the gases/liquids inside the cell from leaking and polymers are usually used for the seal or gasket materials. They in general possess the viscoelastic property which induces stress relaxation of the material under constant strain. The stress relaxation behavior of liquid silicone rubber, a type of polymer used as seals in PEMFCs, is studied in this work. A Prony series is used to predict the compression stress relaxation curve at different strain levels. Applying the time–temperature superposition, master curves are generated and used for predicting the service life of this material as seals in PEMFCs. The estimated lives in water and in air are compared.

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1. Introduction

The PEMFC is a potential and promising power source for portable, stationary, and automotive applications because of its high efficiency and clean reactants. Of importance to any commercial product is the durability and according to US Department of Energy, PEMFCs for transportation applications must operate reliably for at least 5000 h at a temperature range from -40 to 80 °C [1]. To satisfy this requirement, the seals in the PEMFC must be durable enough to bear the load at the normal operation temperature.

These seals may exhibit some of the stress relation characteristics observed and studied in the membranes of PEMFCs. For example, Patankar et al. [2,3] studied the effect of moisture and temperature on the stress relaxation of a Gore-membrane and used non-linear viscoelastic models to characterize these relaxations. Liu et al. [4] investigated the influence of air and water on the stress relaxation of a Nafion[®] 117 membrane at elevated temperatures. Bauer et al. [5] reported that a Nafion[®] 117 membrane in a humid atmosphere has mechanical behavior different from that in a dry condition and they found that water stiffens the membrane at high temperature.

Relatively little work on gaskets or seals in fuel cells had been reported in the literature. Proper design of seals should ensure

not only that it is effective initially, but also that it is sufficiently durable throughout the entire design life of the fuel cell. Field or long term laboratory tests often show that one of the limiting factors in the durability of PEMFCs is the leaking of the liquids and/or gas from inside. This leaking or loss of functionality of seals can be a result of either chemical attack, long term mechanical degradation, or both. For instance, Husar et al. [6] reported gasket failure of a seven-cell stack during thermal cycling. Tian et al. [7] identified an anode/cooling compartment leak that was due to the failure of gaskets. Schulze et al. [8] pointed out that the degradation of seals may introduce decomposed products that can contaminate the catalyst and change the characteristic of the electrodes. For other applications, the long-term stress relaxation behavior of elastomers was quantified using the time–temperature superposition principle by Ronan et al. [9].

Chemical and mechanical degradation of gasket materials in either a model PEMFC environment or a solution designed to simulate accelerated exposure was studied by Tan et al. [10–13]. Gasket materials such as ethylene propylene diene monomer (EPDM) rubber and a fluoroelastomer were first aged in the PEMFC environments. The chemical and mechanical properties were then assessed. Leachants from the gasket materials into the solutions, which may be detrimental to the electrochemical reactions in fuel cell operation, were also studied.

The seal or gasket is typically made of polymeric materials. Polymers are known to have viscoelastic behavior and thus the relationship between stress and strain strongly depends on time. Because of the interaction between the viscosity and elasticity,

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viscoelastic materials show “stress relaxation” if the strain is held constant and “creep” if the stress is held constant. Under constant strain or deformation like in most sealing applications, the retained stress or force in the deformed seal gradually decreases and the material may eventually lose its sealing function.

Stress relaxation of polymers is due to the combination of several factors, namely, physical relaxation, chemical relaxation, and thermal degradation. When subjected to deformation, molecular chains can relocate, which causes physical relaxation. Physical relaxation usually happens at the beginning of the stress relaxation. Chemical stress relaxation, which typically occurs later, and thermal degradation are due to increased movements of the molecular chains at increased temperature, which causes chemical reactions or even chain scission.

In sealing applications, stress relaxation of the polymeric seal after assembly directly reduces the sealing force. The seal would lose its sealing capability when the stress in the seal is lower than certain values, e.g. the internal pressure. Environmental parameters that can affect the stress relaxation behavior of a particular polymeric material include temperature, humidity, and operation cycles.

The present paper is concerned with the stress relaxation behavior of liquid silicone rubber (LSR) at different temperatures. The objective is to provide basic experimental data and to predict the sealing life in PEMFC applications when LSR is used as the seal or gasket material.

Compression stress relaxation tests were performed on LSR in both ambient air and wet conditions, at different applied strain levels, and at elevated temperatures. A stress relaxation model was adopted for this material. The time–temperature superposition (TTS) principle was used at various conditions to form the master curve at selected reference temperatures. Service life of the seals was then predicted based on the master curve.

2. Models

2.1. Viscoelastic model

As discussed above, viscoelastic materials have the properties of both viscosity and elasticity. A mathematical model for viscoelastic behavior therefore would include elements representing both. Typical models, linear or non-linear, include springs and dashpots. The spring is for elastic deformation and it can respond instantaneously to any applied load. The dashpot reacts like viscous fluids, and moves at a rate proportional to the stress.

A basic model, called the Maxwell model, is shown in Fig. 1. It is represented by a dashpot (with the coefficient of viscosity η) and a spring (with a spring constant or Young’s modulus E) connected in series. The stress relaxation solution to the Maxwell model

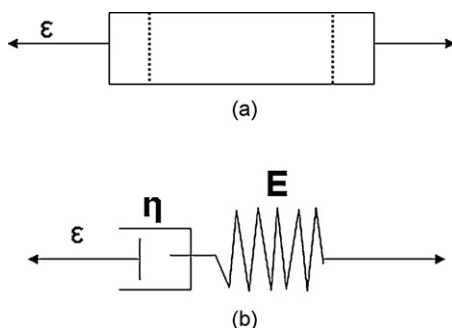


Fig. 1. (a) A viscoelastic material under strain, (b) Maxwell model for the material.

can be written as

$$\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right). \tag{1}$$

where σ_0 is the stress at $t=0$ and τ is the relaxation time. According to this model the stress decays exponentially with time (or relaxation), which is valid for most polymers.

Based on the Maxwell equation, several extensions have been made [14]. For example, Rabinovich [15] used a non-linear Maxwell’s equation to predict the stress relaxation. Alfrey [16] connected the springs and dashpots in parallel to generate a new model to describe the relaxation curve. These models have been successfully applied to predict the stress relaxation behavior of materials at certain conditions. A generalized Maxwell model would result in an equation

$$\sigma(t) = \sigma_\infty + \sum_{i=1}^n \sigma_i \exp\left(-\frac{t}{\tau_i}\right) \tag{2}$$

where σ_∞ is the stress stabilized after a long time, σ_i depends on the applied strain level and material properties and τ_i is a material constant. This equation is often called the Prony series and is the most popular model for stress relaxation of polymeric materials. Practically, only a few terms in Eq. (2) are retained to achieve a desired accuracy.

As shown later, the SLR material studied in this work exhibits nearly linear behavior up to 25% strain which is in the range of interest in PEMFC sealing applications. As a consequence, adoption of the Prony series is justified for the present work.

2.2. Time–temperature superposition

As discussed above, molecular motion in polymeric materials results in stress relaxation. Molecules usually move faster at higher temperature. As a consequence, stress relaxation is, to a large extent, influenced by temperature. For polymeric materials, the time–temperature superposition (TTS) describes the relation between time t and temperature T for its mechanical response [17,18]. It can be written symbolically as shown by Eq. (3),

$$G_r(t, T_2) = G_r(a_T(T_1, T_2)t, T_1) \tag{3}$$

where G_r is mechanical response, which is function of time and temperature, T_1 and T_2 are two different temperatures, t is the time, and a_T is the shift factor determined from experiments.

Fig. 2 demonstrates the TTS process and the shift factor a_T . TTS is a mathematical application of the Boltzmann’s superposition principle. The essence of this principle is that time and temperature are equivalent and therefore, the time function of stress at one temperature has the same shape of the function at another temperature. The stress relaxation curve determined at certain temperature can then be horizontally shifted to another temperature when presented on a logarithmic–logarithmic scale. The beauty of this TTS lies in that it can be used to avoid long-term tests on creep or stress relaxation of polymers at a low temperature, by testing the material

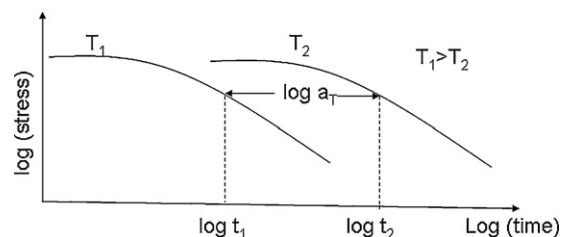


Fig. 2. The schematic of the time–temperature superposition principle.

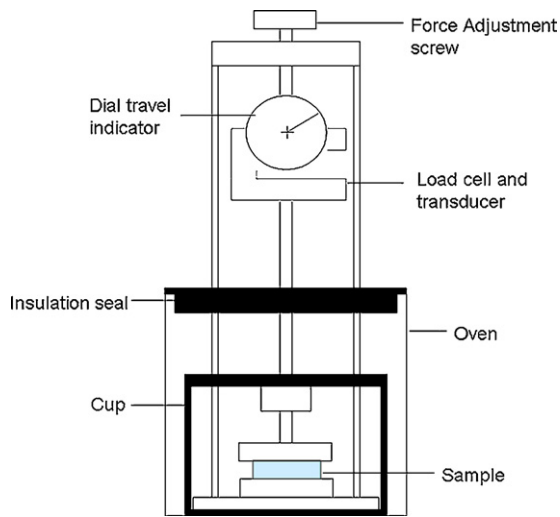


Fig. 3. The schematic of compression stress relaxation rig.

in a short time at a higher temperature. The TTS has been extensively used in studying creep and stress relaxation of polymeric materials [19].

3. Experiments

3.1. Material and preparation

Liquid silicon rubber (LSR), a commercially available high purity platinum-cured silicone, is a good candidate for gasket in PEMFC. It is inexpensive and easy to mould into custom shapes and design. Its glass transition temperature (-40°C) is relatively low and therefore it remains flexible, elastic, and retains its properties up to 300°C . Although its surface chemistry may change over time when exposed to PEMFC environments, its bulk mechanical properties remain unchanged [11]. However, like most polymers, LSR also shows viscoelastic behavior especially at high temperatures. For this work, LSR in sheet form was obtained from a manufacturer and cut into round buttons for compression stress relaxation (CSR) tests.

A cylindrical disc with a 13 mm diameter (D) and 6.3 mm height (H) or a ring with square cross section 2×2 mm and inside diameter 15 mm can be used for stress relaxation tests according to ASTM D6147 [20]. In our experiment, the former was used for convenience. It is worth noting that it is difficult to make the samples perfectly cylindrical when they are directly punched out from sheet material. A tool was designed and used to cut the sample from the sheet to preserve the cylindrical shape.

3.2. Instrument

The stress relaxation equipment was made by Elastocon AB, (Sweden) and this particular model consists of three independent testing rigs. Fig. 3 shows the schematics of a rig. Each rig has a load cell, a fixture to apply a constant deformation to the sample, and a container that can test the sample at a certain temperature. Liquid can be added to the cup or ambient air can be used. The rigs are connected to a data acquisition device. Both the temperature and the resultant force of the specimen can be continuously recorded by a computer throughout the test period.

3.3. Experiments

Table 1 lists the stress relaxation tests performed. They were generally at temperatures higher than the room temperature and

Table 1
Compression stress relaxation tests.

	Temperature ($^{\circ}\text{C}$)	Strain level (%)	Applied stress (MPa)
In ambient air	25	25	1.42
	70	25	1.49
	120	25	1.7
In DI water	70	10	0.56
	70	15	0.86
	70	25	1.24
	100	25	1.34
	120	25	1.44

at various strain levels. The wet condition was achieved by putting de-ionized water (DI water) in the container so the specimen was completely immersed throughout the test. The container had a cover with seals and it can keep the water vapor inside even at high temperature such as 100°C and 120°C . This procedure is validated by the fact that the specimens were still immersed in DI water after completing the test. Sufficient amounts of water were placed into the cell to ensure the sample has immersed at high temperatures.

The test procedure follows the ASTM D6147, such as pre-conditioning of the test specimen and the strain applied at the test temperature. Note that this procedure is at its best useful to study material behavior and compare the relative merits of different materials, but not necessarily to emulate actual service conditions.

4. Result and discussion

4.1. Material model for compression stress relaxation

Fig. 4 shows the stress relaxation curves obtained from strain levels at 10%, 15% and 25% for specimens in DI water at 70°C . In general, they all show a nearly exponential decay of stress with time. The isochronous stress strain curves generated from the data in Fig. 4 are shown in Fig. 5. It can be seen that at times from 0 to 1600 h, the stress is nearly proportional to strain. Therefore, the linearized viscoelastic model, the Prony series shown as Eq. (2), is proved to be adequate for the current work. It is noted that the Prony series can be rewritten as

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = \frac{1}{\varepsilon_0} \left[\sigma_{\infty} + \sum_{i=1}^n \sigma_i \exp\left(-\frac{t}{\tau_i}\right) \right]$$

$$= E_{\infty} + \sum_{i=1}^n E_i \exp\left(-\frac{t}{\tau_i}\right) \quad (4)$$

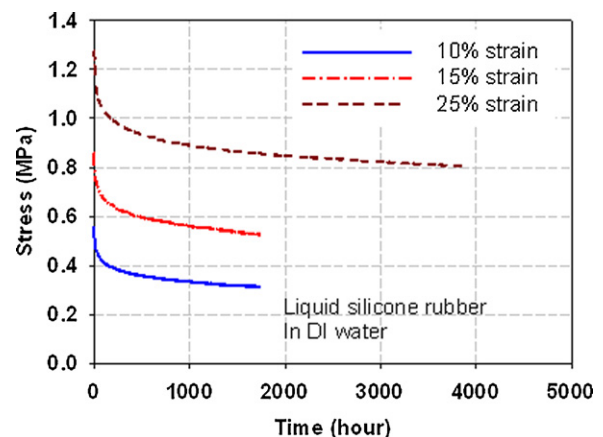


Fig. 4. Stress relaxation curves of LSR at three strain levels, 10%, 15% and 25% in DI water.

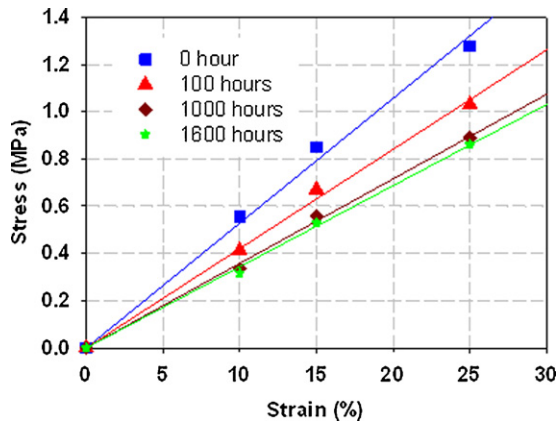


Fig. 5. Isochronous stress–strain plot of LSR at different times.

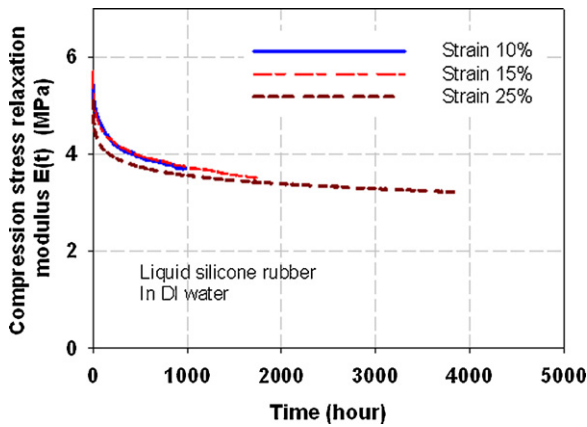


Fig. 6. Time dependent compression stress relaxation modulus $E(t)$ at three different strain levels.

The “Young’s Modulus $E(t)$ ” is therefore a function of time only, regardless of the level of the applied constant strain ϵ_0 . Fig. 6 shows the time dependent Young’s modulus at the three different strain levels. Although the curves at 10% and 15% superimpose very well, the deviation shown by the 25% strain may indicate a slight non-linear dependence. In general this deviation was only slightly larger than the reproducibility error.

The Prony series of Eq. (2) with three exponential terms was selected to fit with the stress relaxation curve at 25% strain. The coefficients in the fitted Prony series are shown in Table 2. Using these coefficients and Eqs. (2) or (4), the stress relaxation curves at 10% and 15% of strain are predicted and shown in Fig. 7. It is seen from Fig. 7 that the predicted and the test data are reasonably close. It indicates that this model is appropriate for this material and three terms are sufficient to describe the stress relaxation of this material at this temperature.

From the practical point of view, these results demonstrate that the test data at one strain level can be transferred or applied to another strain level through the Maxwell model (2) or (4). Therefore, for LSR and convenience only one strain level in stress relaxation tests is required at a given temperature to accurately determine the sealing behavior of PEMFC.

Table 2
The coefficients of three term Prony series.

E_∞ (MPa)	E_1 (MPa)	E_2 (MPa)	E_3 (MPa)	τ_1 (h)	τ_2 (h)	τ_3 (h)
0.770912	0.168802	0.133157	0.176865	18.577	254.065	2500

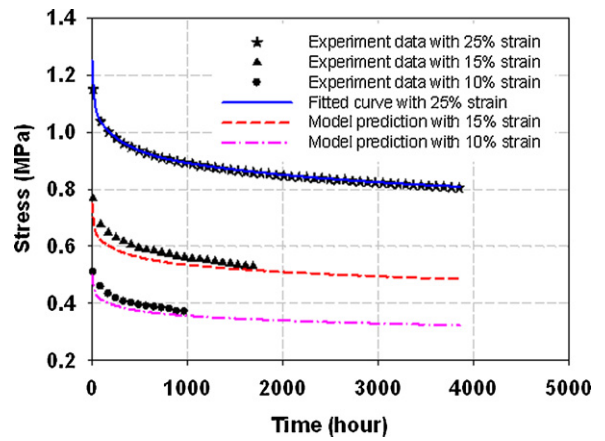


Fig. 7. Compression stress relaxation – a comparison of test data with prediction from the linear viscoelastic model.

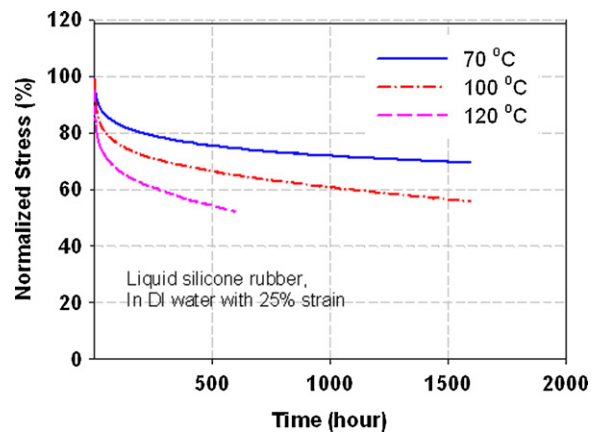


Fig. 8. Stress relaxation data of liquid silicone rubber in DI water at three temperatures and at 25% strain.

4.2. Compression stress relaxation test results with specimens in DI water

Fig. 8 shows the normalized stress relaxation curves at three temperatures, 70 °C, 100 °C, and 120 °C, all with 25% applied strain. These were normalized with the initial stress. The tests for 70 °C and 100 °C were terminated after about 1600 h, since the relaxation rate at this time is sufficiently low. Specifically, the incremental relaxation rate at 1600 h is at 0.0038%/h for the case of 70 °C and 0.0052%/h for the case of 100 °C which would introduce no significant additional relaxation afterwards. For instance, in another 1000 h after these 1600 h, the additional stress relaxation would be less than 3.8% and 5.2%, respectively, for the two cases. It is noted that the test at 120 °C was stopped at around 600 h due to premature leakage of the high pressure water vapor in the container. Test data in Fig. 8 indicates the exponential decay nature of the stress with time similar to that described by the Maxwell model. It also shows that higher temperatures contribute to faster stress relaxation.

Fig. 9 shows the same data as in Fig. 8; but with a logarithmic scale. The linearity of the 70 °C curve indicates that physical relax-

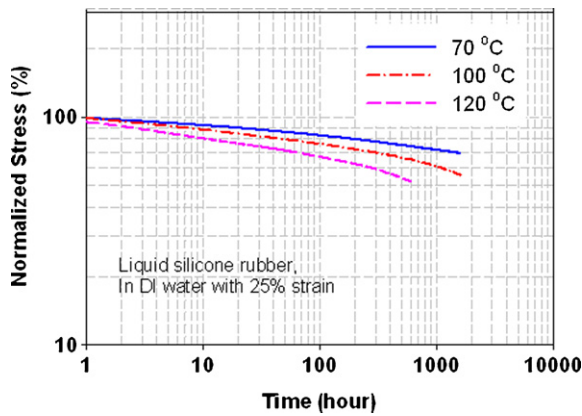


Fig. 9. Stress relaxation data of liquid silicone rubber in DI water at three temperatures in logarithmic scale.

ation is observed throughout the test time. The linearity for the 100 °C curve stops at about 700 h. After that, the data gradually deviated from the linearity indicating chemical relaxation. The linear region for the 120 °C curve is limited to about 400 h. These data demonstrate that chemical relaxation is prone to occur at higher temperature [21].

With TTS, the curves in Fig. 9 are shifted to construct the master curve in Fig. 10 at a reference temperature of 70 °C. In this figure, the three curves at the different temperatures overlapped, indicating good agreement with the master curve at this particular reference temperature.

According to the equivalence between time and temperature, the master curve at one temperature can be shifted horizontally to another temperature by using the shift factor. The shift factor for this material was generated and is presented in Fig. 11 on a logarithmic scale and it can be used to shift the master curve from the one in Fig. 10 to another temperature. Note the direction of the horizontally shift is determined by the sign of $\log a_T$. If the shift factor is larger than 1, the shift would be towards the origin and if it is smaller than 1, the shift would be away from the origin. When the temperature is much higher than 70 °C, the shift factor increases sharply in Fig. 11. This indicates that high temperature exerts a considerable effect on the compression stress relaxation.

Practically, to avoid tedious long time tests, e.g. years, for service life prediction, laboratory tests are typically conducted within a reasonable test time, e.g. weeks, at a higher temperature than the operating temperature. Then, by applying the TTS principle, the test curve at higher temperature can be shifted to a lower temperature,

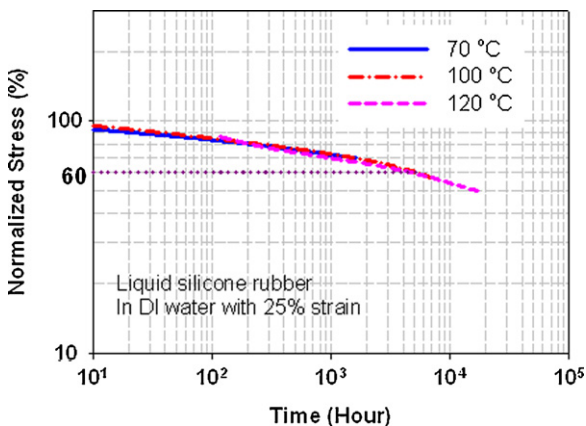


Fig. 10. Master curve of stress relaxation of LSR at a reference temperature of 70 °C.

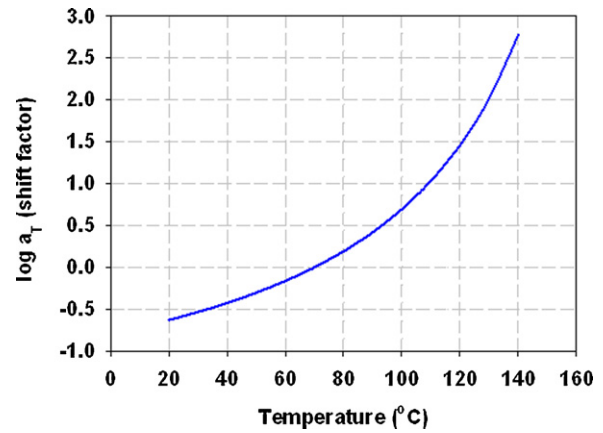


Fig. 11. Shift factor of master curve in DI water with reference 70 °C.

e.g. the operating temperature, corresponding to a longer test time. This is the beauty of TTS.

For example, assuming the LSR is used as the seal in FC and the operating temperature is at 70 °C, the service life of the seal would be predicted around 5000 h (6.9 months) from Fig. 10, if 60% of the initial sealing stress has to be maintained. In this example, we have set the criterion that a resulting seal stress less than 60% of its initially applied stress will induce leakage. The choice of this cutoff percentage or stress obviously depends upon the internal pressure of the FC and other practical considerations.

4.3. Compression stress relaxation test results with specimens in ambient air

LSR specimens were also tested in ambient air at three temperatures, i.e. 25 °C, 70 °C and 120 °C, with 25% applied strain. Fig. 12 shows the stress relaxation test data. The trend shown in this figure is similar to the data in DI water. At the beginning of the test, stress relaxed quickly and higher temperatures result in faster stress relaxation. A slight variation is seen in the curve at 25 °C which is believed to come from the variation of the ambient temperature in the room as the test was done outside an oven. This nevertheless should not affect the shifted master curve as discussed in the next paragraph.

Applying TTS, a master curve at 70 °C is constructed and shown in Fig. 13 and the shift factor of the master curve to other temperatures is presented in Fig. 14 on a logarithmic scale. Again, assuming

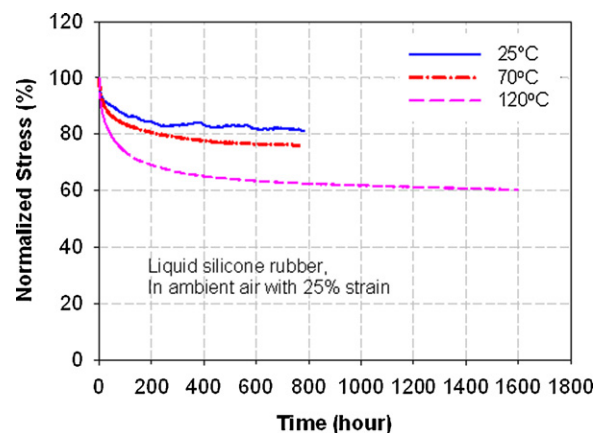


Fig. 12. Stress relaxation test data of LSR at three different temperatures in ambient air.

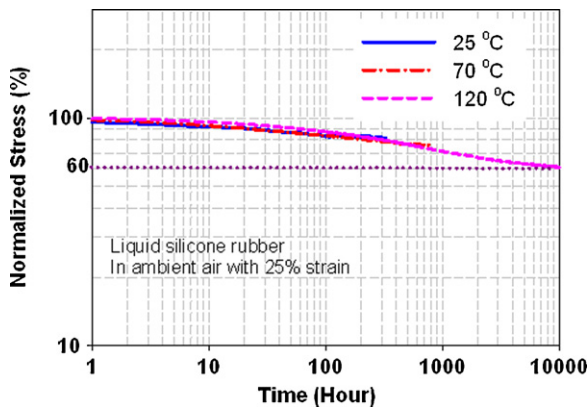


Fig. 13. Master curve of stress relaxation of LSR in ambient air at a reference temperature of 70 °C.

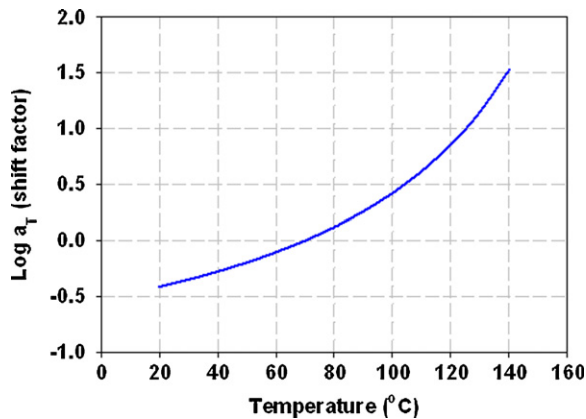


Fig. 14. Shift factor of master curve in ambient air with reference 70 °C.

60% of the initial sealing stress must be maintained for effective sealing, data in Fig. 13 predict that the life to reach this condition is about 9000 h (12.5 months).

4.4. Comparison of the stress relaxation results in DI water and ambient air

The above two sections discussed the stress relaxation behavior of LSR in air and DI water. Both showed that temperature plays a crucial role in the stress relaxation. In addition, it appears the media, in which the specimens are exposed to, can also affect the relaxation rate. For example, as discussed in previous sections the service life of LSR as a seal at 70 °C is predicted to change from 5000 h (6.9 months) in DI water to 9000 h (12.5 months) in ambient air conditions, if 60% of the sealing force is to be retained. Water seems to be detrimental to the stress relaxation of this liquid silicone rubber material at 70 °C. It is suspected that water accelerates the chemical degradation of the sample. Further tests are needed to confirm this conjecture.

5. Conclusion

This paper presents experimental studies of liquid silicone rubber (LSR), which is a promising gasket material in PEMFCs. The stress relaxation behavior of LSR in DI water and ambient air was presented for different temperatures and different applied strain levels. From the experimental data and analysis, it is concluded:

1. A linear model represented by the Prony series with three terms is sufficient for describing the stress relaxation of this material.
2. Applying the time–temperature superposition (TTS) principle, master stress relaxation curves can be constructed for any temperature.
3. The master curves can be used to estimate the service life of the LSR seal when a cutoff criterion is specified.
4. It appears that the medium, in which LSR is exposed, also plays an important role in stress relaxation of the material.

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References

- [1] US Department of Energy, in: Hydrogen, Fuel Cells & Infrastructure Technologies Program, 2007, p. 7.
- [2] K.A. Patankar, D.A. Dillard, S.W. Case, M.W. Ellis, Y.H. Lai, M.K. Budinski, C.S. Gittleman, *Mechanics of Time-Dependent Materials* 12 (2008) 221–236.
- [3] K. Patankar, M.W. Ellis, M. Budinski, S.W. Case, Y.-H. Lai, C. Gittleman, in: *The 7th International Conference on Fuel Cell Science, Engineering and Technology*, Newport Beach, CA, 2009.
- [4] D. Liu, M.A. Hickner, S.W. Case, J.J. Lesko, *Journal of Engineering Materials and Technology-Transactions of the ASME* 128 (2006) 503–508.
- [5] F. Bauer, S. Denzler, M. Willert-Porada, *Journal of Polymer Science, Part B: Polymer Physics* 43 (2005) 786–795.
- [6] A. Husar, M. Serra, C. Kunusch, *Journal of Power Sources* 169 (2007) 85–91.
- [7] G.Y. Tian, S. Wasterlain, D. Candusso, F. Harel, D. Hissel, X. Francois, *International Journal of Hydrogen Energy* 35 (2010) 2772–2776.
- [8] M. Schulze, T. Knori, A. Schneider, E. Gulzow, *Journal of Power Sources* 127 (2004) 222–229.
- [9] S. Ronan, T. Alshuth, S. Jerrams, N. Murphy, *Materials & Design* 28 (2007) 1513–1523.
- [10] J.Z. Tan, Y.J. Chao, M. Yang, W.K. Lee, J.W. Van Zee, *International Journal of Hydrogen Energy* (2010) 1–7.
- [11] J.Z. Tan, Y.J. Chao, J.W. Van Zee, W.K. Lee, *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 445 (2007) 669–675.
- [12] J.Z. Tan, Y.J. Chao, J.W. Van Zee, X.D. Li, X.N. Wang, M. Yang, *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 496 (2008) 464–470.
- [13] J.Z. Tan, Y.J. Chao, X.D. Li, J.W. Van Zee, *Journal of Power Sources* 172 (2007) 782–789.
- [14] T.M. Junisbekov, V.N. Kestelman, N.I. Malinin, *Stress Relaxation in Viscoelastic Materials*, Science Publishers, Enfield, NH, 2003.
- [15] A.L. Rabinovich, *Introduction to the Mechanics of Reinforced Polymers*, Moscow, 1970.
- [16] T. Alfrey, *Mechanical Properties of High Polymers*, Moscow, 1952.
- [17] P.C. Hiemenz, T. Lodge, *Polymer Chemistry*, 2nd ed., CRC Press, Boca Raton, 2007.
- [18] R.D. Andrews, A.V. Tobolsky, *Journal of Polymer Science* 7 (1951) 221–242.
- [19] L.C.E. Struik, *Physical aging in amorphous polymers and other materials*, Elsevier Scientific Pub. Co., Distributors for the U.S. and Canada, Elsevier North-Holland, Amsterdam, New York, 1978.
- [20] ASTM D6147, in: *ASTM International*, West Conshohocken, PA, 2002.
- [21] C.J. Derham, *Plastic Rubber and Composites Proceeding and Applications* 26 (1997) 130–136.