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Short communication

Evaluating the time and temperature dependent biaxial strength of Gore-Select® series 57 proton exchange membrane using a pressure loaded blister test

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ABSTRACT

Temperature and humidity fluctuations in operating fuel cells impose significant biaxial stresses in the constrained proton exchange membranes (PEMs) of a fuel cell stack. The strength of the PEM, and its ability to withstand cyclic environment-induced stresses, plays an important role in membrane integrity and consequently, fuel cell durability. In this study, a pressure loaded blister test is used to characterize the biaxial strength of Gore-Select® series 57 over a range of times and temperatures. Hencky's classical solution for a pressurized circular membrane is used to estimate biaxial strength values from burst pressure measurements. A hereditary integral is employed to construct the linear viscoelastic analog to Hencky's linear elastic exact solution. Biaxial strength master curves are constructed using traditional time–temperature superposition principle techniques and the associated temperature shift factors show good agreement with shift factors obtained from constitutive (stress relaxation) and fracture (knife slit) tests of the material.

1. Introduction

Strength characterization of proton exchange membranes (PEMs) is critical for lifetime prediction of the membranes in fuel cell applications. The Department of Energy has set durability goals for PEM transportation applications at a 5000 h service life by 2015 [1]. These goals would hold PEM fuel cell vehicles to the same service life standards of today's current internal combustion engine systems. However, current fuel cell demonstration vehicles have yet to reach the DOE target [2]. One reason is that under operating conditions and due to non-continuous usage, the fuel cell environment experiences both temperature and humidity fluctuations. When exposed to such hygrothermal changes, the membrane, which is clamped along the lands and seal gasket of fuel cells and constrained by the catalyst and gas diffusion layers, is expected to be under biaxial stresses. Lai et al. has shown that these imposed cyclic stresses can initiate crack formation, which leads to gas crossover and subsequent fuel cell failure [3]. In a previous work, Dillard et al. [4] showed that pressure loaded blister testing is a viable method to impose these biaxial stress states experimentally and Li et al. reported the use of pressure-loaded blisters to characterize the fatigue and creep to leak behaviors of PEMs [5]. In particular, pressure-ramped blister testing provides biaxial leakage or burst strength estimates which could be more descriptive of failure modes seen in working fuel cells than traditional strengths obtained by uniaxial tensile testing. Since biaxial burst strength values could provide insight into evaluating membrane durability, a means of experimentally and analytically obtaining these values while incorporating accurate material behavior is desired.

In early work with pressurized circular membrane testing, Hencky showed that stresses within the pressurized blister could be exactly determined for a linear elastic, homogeneous, isotropic membrane, using a power series solution [6]. The radial and tangential stresses, σ_r and σ_θ, respectively, are given [6,7] as:

$$\begin{aligned}\sigma_r(r) &= \frac{1}{4}\left(\frac{Ep^2a^2}{h^2}\right)^{1/3}\cdot\sum_{k=0}^{\infty}B_{2k}\left(\frac{r}{a}\right)^{2k}\\ \sigma_\theta(r) &= \frac{1}{4}\left(\frac{Ep^2a^2}{h^2}\right)^{1/3}\cdot\sum_{k=0}^{\infty}(2k+1)B_{2k}\left(\frac{r}{a}\right)^{2k}\end{aligned} \tag{1}$$

where E is the elastic modulus of the material, p is the applied pressure, a is the free radius of the blister, h is the thickness of the blister, and B_{2k} is the coefficients to be determined through application of boundary conditions. By assuming zero residual mechanical strain, a reasonable approximation of σ_r and σ_θ at the center of a

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pressurized PEM blister test is given by,

$$\sigma_r = \sigma_\theta = \frac{B_0}{4}\left(\frac{Ep^2a^2}{h^2}\right)^{1/3} \tag{2}$$

where $B_0 \approx 1.777$ for an assumed Poisson's ratio value of $\nu = 0.4$. Since Hencky's solution assumes a linear elastic material, modifications are needed to address the viscoelastic nature of polymers like PEM. To accurately explore time and temperature dependence of biaxial strength, material behavior due to environmental conditions must also be considered.

2. Theory

The viscoelastic response of polymers such as PEMs exhibits a dependence on temperature, time, and humidity. Early work with polymers led to the introduction of the time–temperature superposition principle (TTSP), which allows for the transformation of data from one temperature to another via horizontal shifts on a logarithmic time axis [8]. Alternately, short term viscoelastic properties such as relaxation modulus collected at different temperatures can be superimposed into a master curve describing behavior at times both shorter and longer than experimentally accessible. However, as noted in [8], the simple TTSP is not applicable to all polymers. Relevant to this study, success has been demonstrated in applying TTSP to Gore-Select® series 57. Specifically, Patankar et al. [9] studied the effects of both temperature and humidity on Gore-Select® series 57 and presented an initial linear viscoelastic characterization in the form of a relaxation modulus master curve along with hygrothermal shift factors.

The behavior of these viscoelastic membranes as relevant to our study is illustrated in Fig. 1, as a plot of the Prony series approximation of the relaxation modulus master curve obtained from stress relaxation tests conducted on the Gore-Select® series 57 membranes tested in a dynamic mechanical analyzer (DMA) as presented in [9]. It is important to note that the data of Fig. 1 was collected under dry conditions to best simulate the uncontrolled humidity of the high temperature blister tests conducted above and is not identical to the curve presented in [9]. The regions denoted on the plot show the modulus variations within the time and temperature ranges of interest to this study.

It has been shown that the elastic–viscoelastic correspondence principle can be used to derive linear viscoelastic solutions from known linear elastic solutions provided the geometries and boundary conditions are identical [10]. Also known as Alfrey's correspondence principle the process of obtaining these linear viscoelastic solutions is described in detail in [11]. Each traction or displacement variable appearing in the analogous elastic solution is replaced by the Laplace transform of that variable. Next, any elastic constant appearing in the solution is replaced by the product of the Laplace variable s and the Laplace transform of the time dependent analog to the elastic constant. Having now obtained the linear viscoelastic solution in the Laplace domain, we then take the inverse transform to complete the procedure and provide the analogous, time dependent, linear viscoelastic solution. In application to Hencky's solution described above, the only variable requiring transformation into the Laplace domain is the applied pressure. Similarly, the only elastic constant appearing directly in Hencky's solution is the Young's modulus, E, whose corresponding time dependent viscoelastic property is the stress relaxation modulus $E(t)$. Although this principle is typically presented in traditional textbook examples, such as simple shaft torsion, this methodology has been shown broadly useful in solving more complex mechanics problems, such as in the indentation field [12,13].

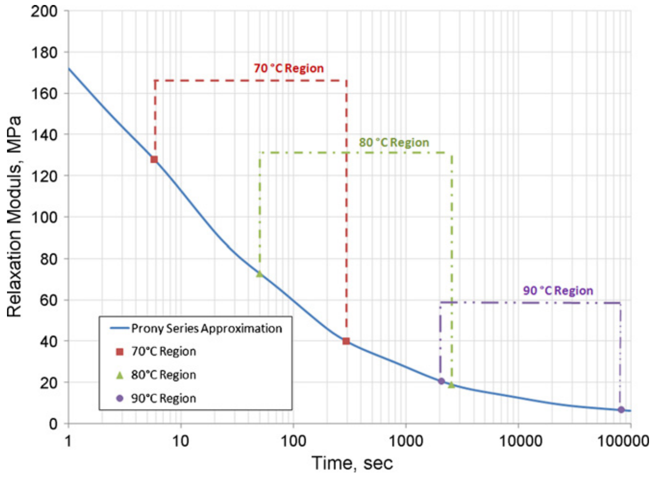

Fig. 1. Plot of Prony series approximation of the relaxation modulus obtained from DMA tests of Gore-Select® series 57 under dry conditions with temperature regions denoted as applicable to the time range of the data utilized in this study.

In applying the correspondence principle to Eq. (2) and taking the inverse Laplace transform, one obtains a hereditary integral formulation in which the stress relaxation modulus, $E(t)$, is convoluted with the pressure input as the only other time dependent parameter. These modifications give σ_r and σ_θ at the center of a pressurized PEM blister as

$$\sigma_r(t) = \sigma_\theta(t) = \frac{B_0}{4}\cdot\left(\frac{a}{h}\right)^{2/3}\int_{-\infty}^{t}(E(t-\beta))^{1/3}\cdot\frac{d\,[p^{2/3}(\beta)]}{d\beta}d\beta \tag{3}$$

Building upon the above concepts, the objective of this study is to characterize the biaxial burst strength of Gore-Select® series 57 PEM over a range of time and temperature values using a pressurized blister test. A hereditary integral formulation of Hencky's classical solution will be employed using stress relaxation data obtained from the methodology in [9]. The TTSP will be independently applied to the collected data and the temperature shift factors obtained will be compared to the shift factors collected from constitutive (stress relaxation) and fracture (knife slitting) tests as described in [9,14]. From application of TTSP, master curves will be generated that describe the effects of time and temperature on biaxial burst strength.

3. Experimental procedure and analysis

The pressurized blister testing method employed for PEMs in previous work [4] was expanded in this study to incorporate a range of test temperatures in order to investigate the applicability of the TTSP in pressure loaded blister tests over temperatures relevant to operating fuel cells. Specifically, tests were conducted on Gore-Select® series 57 (Gore Fuel Cell Technology, Elkton, MD) at temperatures of 70, 80, and 90 °C and readings of the pressure at burst and elapsed time at burst were collected. The experimental procedure, including sample preparation, heating to the desired test temperature, and pressurizing until bursting occurs, was described in detail in [4] and is only briefly reiterated here. Gore-Select® series 57 is an 18 μm-thick version of the perfluorosulfonic acid (PFSA) proton exchange membrane with a layer of micro-reinforced, composite expanded polytetrafluoroethylene (ePTFE). These micro-reinforced membranes have been shown to have improved tear resistance and dimensional stability compared to homogeneous cast membranes under some conditions [5,15,16]. Gore-Select® series 57 membrane, as received, is sandwiched between two backings. One backing was removed before specimen preparation, while the other backing was retained throughout specimen fabrication to form consistent samples. Circular specimens were constructed using the front ferrules of standard Swagelok® tube fittings. A thin coat of Devcon® two-part 5-min epoxy was applied on the rim of the front ferrules, which were then inverted and placed onto a sheet of the membrane. After curing at room temperature, individual specimens were cut out using a razor blade, the second backing was removed, and the specimens were placed in a desiccator until specimen testing. To mount a specimen in preparation for testing, the front ferrule supporting a just taut membrane was placed into a Swagelok® ferrule nut and the assembly was screwed onto a Swagelok® reducing union. Once mounted on the pressure line, specimens were placed in an oven for environmental control and were pressurized using a KDScientifc® Series 230 syringe pump with atmospheric air as the working fluid. A schematic of the experimental setup is shown in Fig. 2a and a photograph of the test in progress is shown in Fig. 2b, respectively.

Raw pressure versus time data were collected from each test, where test initiation was marked by the first noticeable increase in pressure reading and bursting was denoted by catastrophic pressure loss. Successful testing of catastrophic burst failures was also verified in a qualitative way by the audible popping noise that accompanied such failures. Raw data from a representative sample is plotted as pressure versus time in Fig. 3.

From the collected readings from similar tests, burst pressures and times to failure were obtained for a series of syringe displacement rates and test temperatures. For the analysis of this data, Eq. (3) was utilized extensively using temperature appropriate relaxation modulus data given by the Prony series approximation for Gore-Select® series 57 presented in Fig. 1. Although this approach proves to be a vast improvement over the assumptions of linear elastic behavior within the classical Hencky solution, it is imperative to objectively recall assumptions made in formulating this analogous linear viscoelastic solution. In the procedure, the relaxation modulus $E(t)$ was the only time dependent material property used in the modification and was convoluted in the integral with the applied pressure as a function of time, $p(t)$. Admittedly, the thickness will also be a time dependent parameter as the membrane continues thinning throughout the duration of the test. However, appropriate treatment of the thickness becomes quite complicated as it would involve not only applied stress levels at each instant in time but also a viscoelastic characterization of Poisson's ratio, $\nu(t)$, which is not well known or published for Gore-Select® series 57. To significantly reduce computational efforts, a constant value for the thickness of the membrane was assumed.

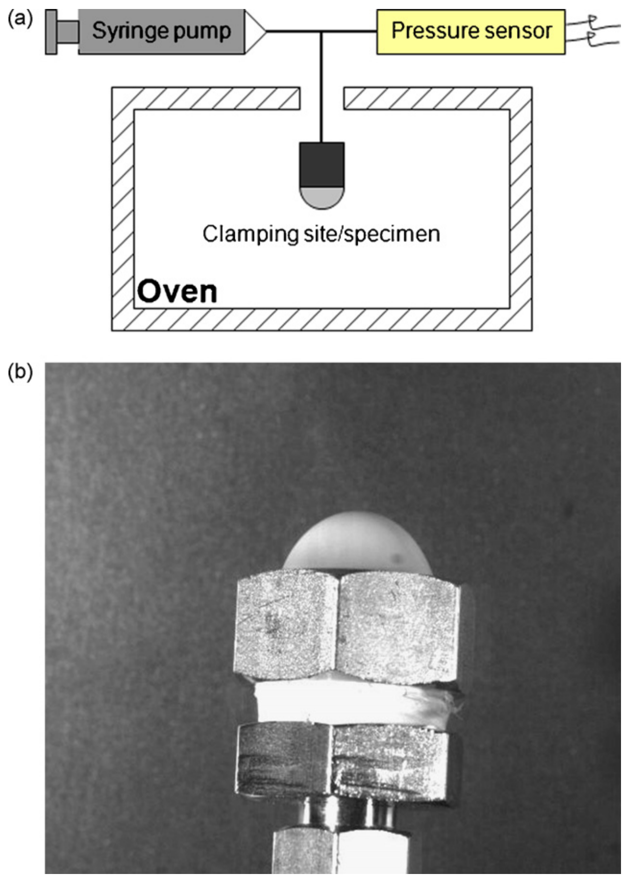

Fig. 2. Illustrations of (a) experimental schematic diagram and (b) blister test in progress [4].

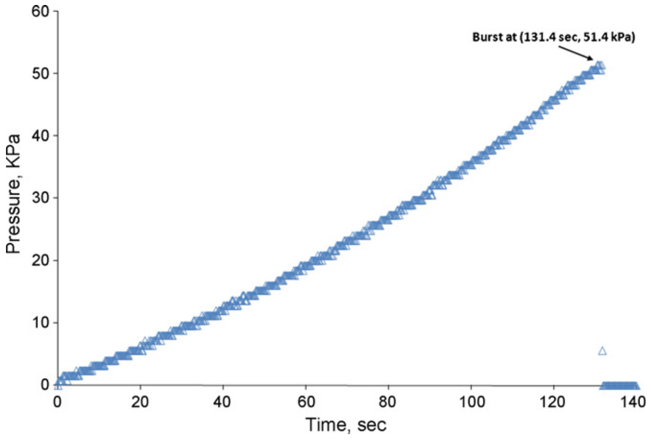

Fig. 3. Raw pressure versus time data from representative sample of a Gore-Select® series 57 blister test conducted at 80 °C with a syringe pump infusion rate of 12 mL min^{-1}. Associated time and pressure at burst are illustrated.

The motivation behind developing and employing this hereditary integral formulation was not just based on a desire to incorporate the time dependent relaxation modulus. The primary reason resulted from anomalous results found from an attempted application of TTSP to data obtained with an assumed constant elastic modulus. The results were temperature shift factors that were surprisingly large, approximately twice the values obtained from DMA testing. It was known that as the hereditary integral formulation accounts for time dependency of the relaxation modulus, the overall slope of the biaxial burst strength versus time curve would become larger in magnitude compared to data with assumed constant elastic modulus. In application of TTSP, the steeper slopes of the hereditary integral method required less horizontal shifting to

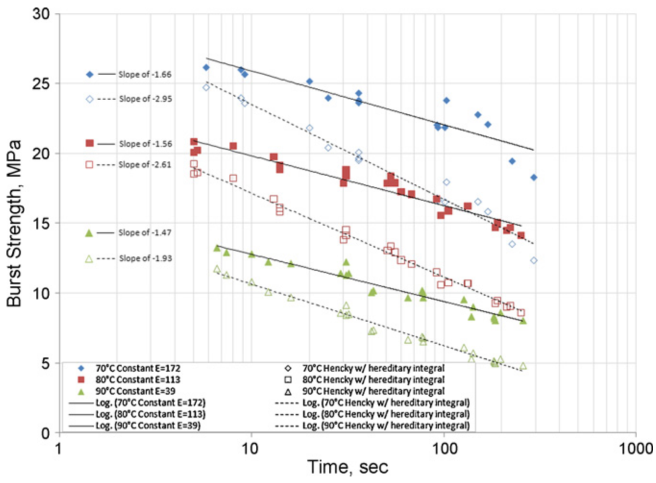

Fig. 4. Comparison of slopes in curves obtained via constant elastic modulus and Hencky with hereditary integral methods.

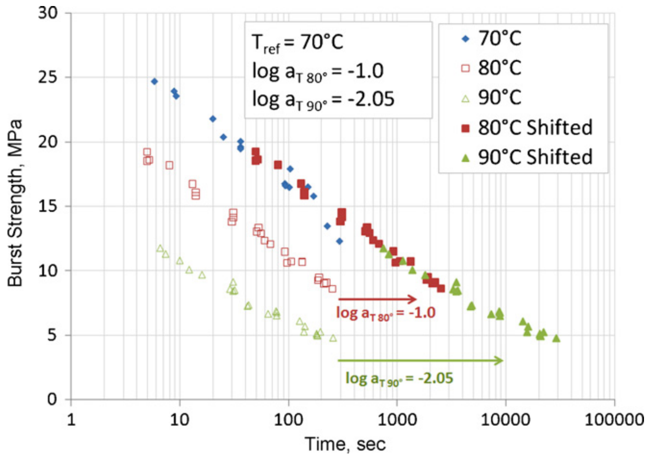

Fig. 5. Burst strength data, calculated via Hencky's solution with a hereditary integral, shifted to form a master curve of Gore-Select® series 57 obtained using traditional shifting methods and referenced at 70 °C.

obtain overlap, thereby reducing the size of the temperature shift factors. This key concept of shift factor difference due to general slope difference is presented visually in Fig. 4.

The data reduction process outlined above provided a set of burst strength versus time to failure curves at selected temperatures. Traditional shifting methods were utilized to form a burst strength master curve with a reference temperature of 70 °C. Temperature shift factors generated were then compared to shift factors obtained by stress relaxation and published knife slit tests in [14] under dry conditions to evaluate consistency.

4. Results and discussion

Application of the hereditary integral to Hencky's solution led to a collection of burst strength values and associated times to failure over the temperature regions of interest. This data was then shifted using the traditional method of choosing a reference data set and sliding subsequent data sets horizontally on a logarithmic time axis until visual alignment with the previous data set was obtained. No vertical shifts were employed. This method of visual shifting was used with a chosen reference temperature of 70 °C to form the burst strength master curve featured in Fig. 5.

As mentioned previously, the use of a hereditary integral with Hencky's solution gives an exact linear viscoelastic solution and is considered an improvement over the constant modulus approach. For completeness, a comparison plot of the burst strength master curves obtained via hereditary integral formulation of Hencky's solution and constant modulus approach is shown in Fig. 6.

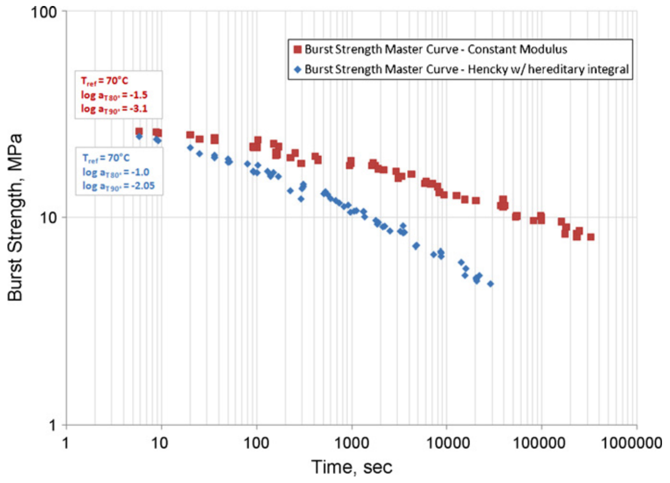

Fig. 6. Comparison plot of burst strength master curves based on both Hencky's solution with a hereditary integral and constant modulus stress analysis methods.

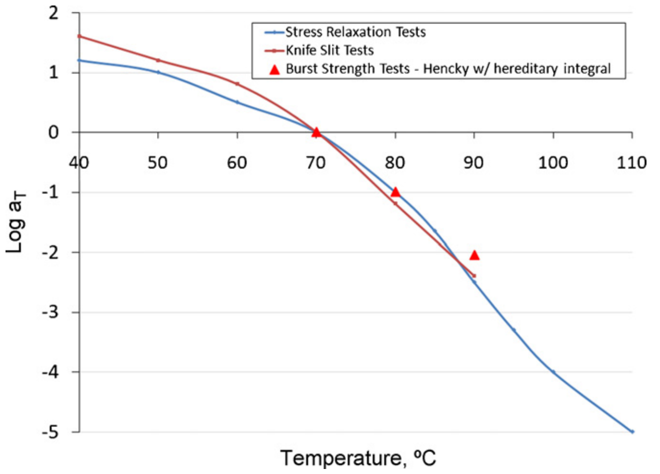

Fig. 7. Plot of temperature shift factors obtained using methodology from [9,14] for stress relaxation and knife slit tests and compared with shift factors obtained in this study.

Table 1
Table of temperature shift factors obtained using methodology from [8,13] for stress relaxation and knife slit tests and compared with shift factors obtained in this study.

	70 °C	80 °C	90 °C
Stress relaxation tests	(Reference)	−1.00	−2.50
Knife slit tests	(Reference)	−1.20	−2.40
Burst strength tests—Hencky W/hereditary integral	(Reference)	−1.00	−2.05
Burst strength tests—Hencky W/constant modulus	(Reference)	−1.50	−3.10

One criterion for evaluating the appropriateness of TTSP is the consistency of shift factors obtained for different material properties [17]. It is therefore encouraging to note that in comparisons of these results with published shift factors obtained from stress relaxation tests and knife slitting tests, the Hencky solution with hereditary integral was found to be in reasonable agreement [9,14]. This suggests that the same molecular relaxation processes that govern stress relaxation behavior and fracture in membranes also control the time dependent failures during biaxial loading. Fig. 7 and Table 1 illustrate, in graphical and tabular forms, the agreement of the different temperature shift factors obtained for Gore-Select® series 57. Development of a burst strength master curve that provides shift factors comparable to those obtained from shifting constitutive data confirms the appropriateness of a viscoelastic framework for characterizing PEM behavior and suggests the possibility of basing lifetime prediction efforts on such accelerated tests. Although shift factor agreement does not guarantee success, it does support attempts to extend strength-life curve results from short time scales into longer lifetime investigations. This is the focus of an ongoing study.

5. Conclusions

Pressure loaded blister tests were used to characterize the biaxial strength of commercially available Gore-Select® series 57 membrane over a range of times to burst and temperatures of interest. The time temperature superposition principle was used to obtain biaxial strength master curves using the traditional visual shifting method on data reduced via the Hencky solution with both a constant modulus and a hereditary integral linear viscoelastic solution; the resulting shift factors from the hereditary integral method were quite consistent with temperature shift factors obtained from stress relaxation and knife slitting tests.

While considering the encouraging insight and progress gained from this study, it is important to recall that the data reduction relies heavily on the linear viscoelastic material characterization from stress relaxation tests. This characterization, which provides no insight into nonlinear or elastic–plastic material properties, is still utilized in this study to treat a problem that likely involves both nonlinearity and plasticity. Although success was achieved via temperature shift factor agreement, the burst strength values presented are likely lower than the true values would be due to localized plasticity and the material nonlinearity. In spite of these approximations and omissions, the methodology is still useful as a cost- and time-effective tool in better understanding and improving PEM in operating fuel cells. In particular, these tests can be used to quickly screen membranes and compare the biaxial burst strength of one material to another. This data can also be used to investigate the critical issue of membrane durability and reliability. Repeated trials at identical loading rates can be used to begin statistical strength studies leading to material reliability constants based on an assumed statistical distribution. Additionally, a burst strength master curve under ramped pressure conditions can lend insight into possible relationships between applied stress levels and subsequent times to failure. Given a suggested relationship for time to failure as a function of applied stress, a damage evolution law can be applied and experimental failures under given loading conditions can be predicted. The ability to develop these techniques in such a simple and time-effective test would be invaluable if proven to predict more complex loading histories. If these efforts in lifetime prediction model are pursued and demonstrated with success, membrane durability could be investigated quickly and play a crucial role in achieving the DOE service life targets [18]. As another component to be added to this study, a similar characterization could be performed over a range of temperatures and relative humidities simultaneously to evaluate the hygrothermal dependence of the biaxial strength of Gore-Select® series 57. Finally, extending all of the applications mentioned into comparative studies of other commercially available membranes would provide valuable insight into behavioral differences among the products.

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References

[1] U.S. Department of Energy Hydrogen, Fuel Cells & Infrastructure Technologies Program: Multi-Year Research, Development and Demonstration Plan (2007).
[2] J. Garbak, Technology Validation 2007 D.O.E Hydrogen Program Merit Review, Department of Energy (D.O.E.), Washington, DC.
[3] Y.H. Lai, C.K. Mittelsteadt, C.S. Gittleman, D.A. Dillard, Journal of Fuel Cell Science and Technology 6 (2009) 021002–021014.
[4] D.A. Dillard, Y. Li, J.R. Grohs, S.W. Case, M.W. Ellis, Y.-H. Lai, M. Budinski, C. Gittleman, Journal of Fuel Cell Science and Technology 6 (2009) 031014–031021.
[5] Y. Li, D.A. Dillard, S.W. Case, M.W. Ellis, Y.-H. Lai, C.S. Gittleman, D.P. Miller, Journal of Power Sources 194 (2009) 873–879.
[6] H. Hencky, Zeitschrift fur Mathematik und Physik 63 (1915) 311–317.
[7] R.J. Hohlfelder, 1999, Bulge and Blister Testing of Thin Films and Their Interfaces, Ph.D. Stanford University, Stanford.
[8] V.T. Arthur, AIP (1956).
[9] K. Patankar, D.A. Dillard, S.W. Case, M.W. Ellis, Y.-H. Lai, M. Budinski, C. Gittleman, Mechanics of Time Dependent Materials 12 (2008) 221–236.
[10] Y.M. Haddad, Viscoelasticity of Engineering Materials, Springer, 1994.
[11] H.F. Brinson, L.C. Brinson, Polymer Engineering Science and Viscoelasticity an Introduction, Springer Science + Business Media, New York, 2008.
[12] G. Odegard, T. Gates, H. Herring, Experimental Mechanics 45 (2) (2005) 130–136.
[13] M. Sakai, S. Shimizu, Journal of Non-Crystalline Solids 282 (2–3) (2001) 236–247.
[14] K. Patankar, D.A. Dillard, S.W. Case, M.W. Ellis, Y.-H. Lai, M. Budinski, C. Gittleman, Journal of Polymer Science (in review).
[15] S. Cleghorn, J. Kolde, W. Liu, in: W. Vielstich, et al. (Eds.), Handbook of Fuel Cell—Fundamentals, Technology and Applications, John Wiley and Sons, 2003.
[16] C. Gittleman, Y.-H. Lai, D. Miller, Proc. AIChE Annual Meeting Conference Proceedings, Cincinnati, OH, 2005.
[17] J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, NY, 1980.
[18] Energy, U.S.D.O., National Hydrogen Energy Roadmap, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/national_h2_roadmap.pdf, 2002.