Characterizing Fracture Energy of Proton Exchange Membrane (PEM) Using a Knife Slit Test

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Abstract

Pinhole formation in proton exchange membranes (PEM) due to hygrothermal stresses during the operation of a fuel cell can be interpreted as a result of crack formation and propagation. Fracture mechanics is one possible approach to characterizing failure. The goal of this study is to measure the intrinsic fracture energy of various commercially available PEMs. The intrinsic fracture energy has been used to characterize the fracture resistance of polymeric materials with minimal plastic dissipation and the absence of viscous dissipation, and has been associated with the long term durability of polymeric materials where subcritical crack growth occurs under slow time-dependent or cyclic loading conditions. Insights into this limiting value of fracture resistance may offer insights into the durability of PEMs. A knife slit test was conducted to measure the fracture energies close to intrinsic fracture [1]. This study continues the previous work to characterize the fracture resistance of several commercial PEMs [2]. Classical fracture mechanics tests like double edge notch tear (DENT) and trouser-tear tests conducted on polymer films often result in fracture energies of many thousands of J/m^2, not consistent with the apparently brittle failure modes sometimes observed in PEM that have been removed from operating fuel cells. The presence of a sharp knife blade reduces crack tip plasticity, providing fracture energies that may be more representative of the intrinsic fracture energies of thin membranes. An environmental chamber was used to enclose the slitting process so experiments at elevated temperature and moisture levels could be conducted. PEMs (Nafion NRE 211, Ion Power N111-IP, and GoreSelect 57) were tested for fracture energy ($\mathcal{G}_c$) at temperatures ranging from 30-90ºC and at humidity levels varying from dry-90% RH using a humidifier. The slitter maintains a constant angle at the knife tip, and was mounted on an Instron tensile testing machine. The test specimens were tested at different cutting rates of 0.1, 1, 10, 50, and 100 mm/min. Doubly-shifted master curves for fracture energy plotted as a function of reduced cutting rate were constructed. We believe this test could be implemented to compare fracture energies ($\mathcal{G}_c$) of various PEM materials. Although the relationship between $\mathcal{G}_c$ and ultimate mechanical durability has not been established yet, the test method may

hold promise for investigating membrane resistance to tearing in fuel cell environments.

Introduction

Polymer exchange membrane-based fuel cells (PEMFCs) have enjoyed considerable attention from various government and private organizations in their quest to develop a cleaner alternative energy source for stationary, portable, and transportation applications. However, there are still certain barriers which are to be overcome in order to utilize the full potential of the fuel cell. High temperature, dry and moist conditions, humidity cycles impose mechanical and chemical stresses, which raise concerns about the durability and performance of the proton exchange membrane (PEM). The function of these membranes is to allow protons to readily pass through while preventing flow of electrons and reactant gas cross-over. Through-thickness pinholes may form in PEMs because of the factors mentioned above, resulting in gas cross-over that leads to localized heating and mechanical and/or chemical degradation, ultimately resulting in the failure of the fuel cell. Although the formation of a pin-hole can be visualized in terms of crack initiation and propagation, and thus may be understood in a fracture mechanics sense [1].

Previous work reported the use of several techniques to measure the fracture energy, or resistance to crack propagation in PEMs, including the double-edge notch tensile test (DENT), trouser tear test, a couple forms of a knife slitting tests [1]. Significantly lower values of fracture energy were obtained for the knife slitting tests, because the sharp microtome blade used was able to significantly reduce the otherwise substantial plastic deformation resulting in the other tearing tests. This significant reduction in observed fracture energy was associated with the small plastic zone of ahead of the crack tip, which was believed to be of the order of thickness of the membrane (typically 25µm, as opposed to much higher radius of crack tip resulting from other techniques). By lowering the plastic dissipation, the intrinsic fracture energy of the material could be approached, which may give useful insight as to how crack propagates and the nature of brittle fracture earlier observed [1, 2]. Li discussed an improvement to the knife slitting test to eliminate the geometrical change and subsequent effects during cutting, to ensure the consistent crack propagation rate and simplify the analysis [2, 3].

Experimental Technique

The knife slitting fixture used in this study was based on some early work by Lake and Yeoh [4] and Gent [5]. These fixtures were capable of measuring the cutting and tearing energy independently. Gent and co-workers reported that by optimizing the angle between two legs of the specimen and the angle at which the uncut specimen is oriented to the knife, the frictional losses during the cutting process were minimized. They tested various elastomeric and thermoplastic specimens and found that, although a sharp blade effectively reduces the plastic zone ahead of crack tip and maintains a sharp crack tip in elastomers, it is not very effective at limiting the plastic blunting that occurs in ductile thermoplastic films[5, 6].

Dillard et al.[1] modified the original design, eliminating the pulleys, whose frictional effects could have affected the measured forces in the very thin PEM films. Further modifications were made in the design, details of which may be found in paper by Li et al. [2]. In the new knife-slit fixture, the relative positions of the knife and the pins that support the membrane are fixed. Thus a fixed geometry is maintained as the knife cuts the membrane. The knife (Leica #818 microtome blade) is mounted to an Interface Forces ULC load cell (0.5N). The two legs of the membrane were passed over the guide pins and attached to the moving crosshead of an Instron 4505 universal testing machine, which pulled the membrane against the knife at variable rates. Figures 1a and 1b show a schematic illustration of the geometry of the fixture and a photo of the test frame, respectively. One of the advantages of this fixture is that since knife does not move at all, it can be enclosed in an environmental chamber. The chamber can be heated and moist air can be introduced. The chamber was heated with a piece of silicon rubber resistance heater and insulated with polystyrene foam. The humidity was introduced using a two-station humidifier supplied by the Fuel Cell Technologies Inc™. A humidity sensor (Vaisala) was used to monitor the humidity in the chamber. To reduce the condensation in the channels, the humidifier was placed at least at the same height as the chamber.

Lake and Yeoh discussed the equations of cutting and tearing energy based on simple equilibrium of body forces (equation 1), assuming there is no straining in the membrane [4].

$$\begin{aligned} C &= \frac{\langle P \rangle}{h} \\ T &= \frac{2L(1-\cos\theta)}{h} = \frac{\langle P \rangle}{h\cos\theta}(1-\cos\theta) \qquad (1) \\ \mathcal{G}_{slit} &= C + T = \frac{\langle P \rangle}{h\cos\theta} \end{aligned}$$

where $\langle P \rangle$ is the average cutting force, h is the thickness of the membrane, L is the pulling force in each leg, θ is the cutting angle, C and T are the cutting and tearing fracture energies respectively. In deriving the above equations, it is assumed that the crack width is equal to the thickness of the membrane. This assumption may not be true and needs to be verified using scanning electron micrographs. Such a study has not been conducted at this point.

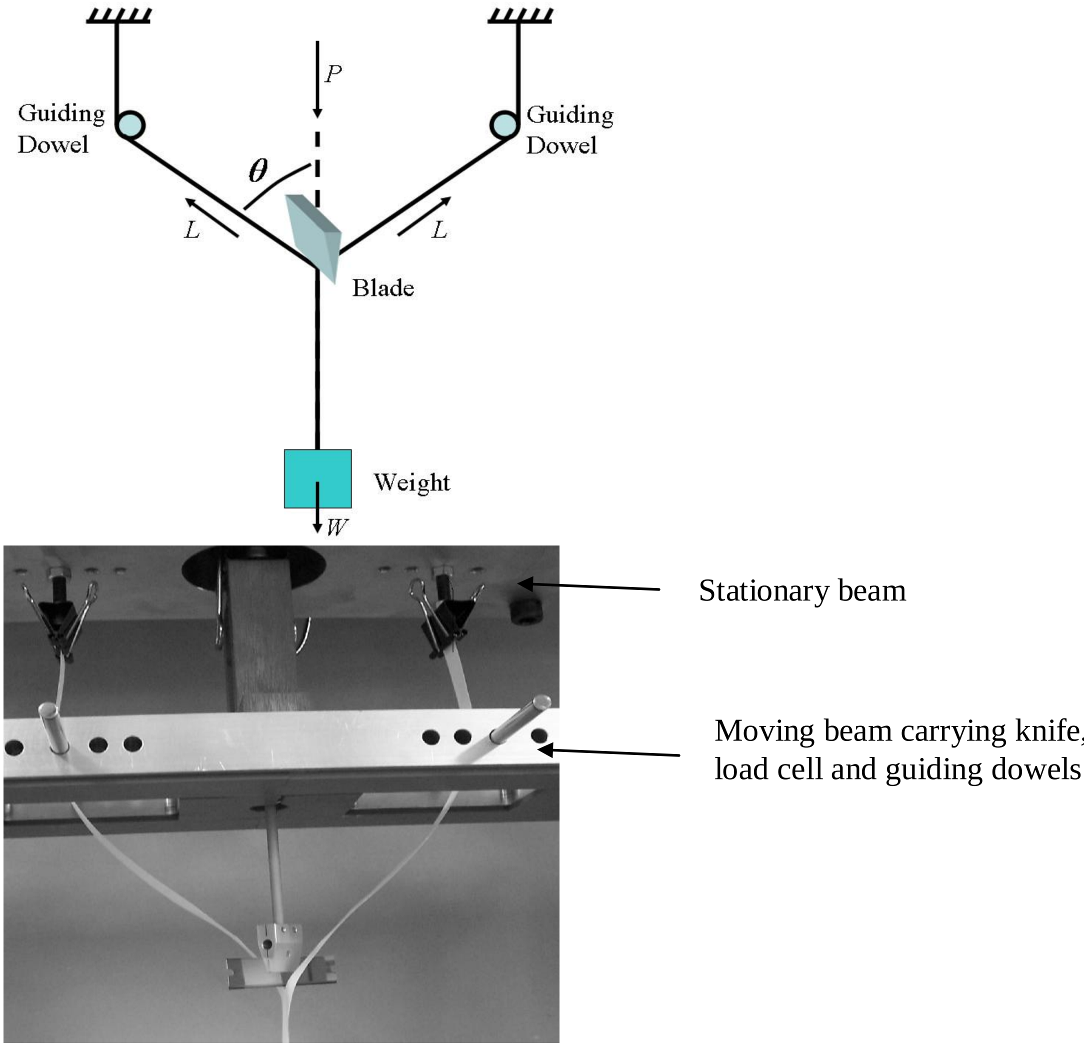

Figure 1. a) Schematic illustration and equilibrium diagram of knife-slit test. The blade and the guiding dowels remain stationary relative to one another (all moving at the same velocity), such that during the cutting process, the cutting angle θ remains constant; b) The test fixture used in the study. By placing the guiding dowels in different holes, tests at different angles can be conducted. A paper sample is used to improve photo clarity. The small load cell is mounted inside the top hole and attached to the support. No weight was hung at the bottom of the sample in this illustrative picture.

Figure 2 shows the dimensions and geometry of the membrane specimens used for experiments. An aluminum template was used to cut the specimen out of the membrane sheet. The template had a slit of the desired length to initiate the precrack in the specimen. A sharp blade was used to cut the edges and a precrack. To reduce usage of the membrane, inexpensive polyester film was cut of the same overall width and length close to the length of a precrack (about 210-215 mm). A small piece of length slightly greater than the uncut section (about 95 mm) and a precrack of about 6 mm were drawn out of the membrane piece. The polyester non-precracked specimen was now stapled with the membrane. Thus the specimen had polyester "legs" which went around the guiding pins, while the knife still cut the membrane.

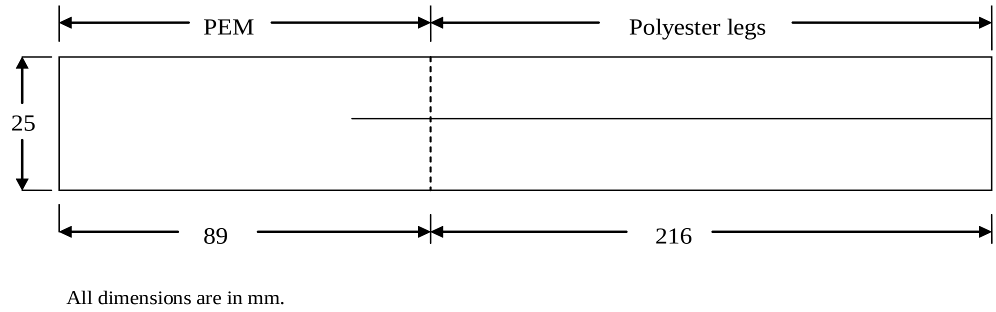

Figure 2. The modified slitting specimen with polyester leaders attached to the membrane to reduce waste.

Results

Membranes were cut at various temperatures and humidity levels to measure the fracture energy. Figure 3 shows a typical load traces for 25µm thick Nafion NRE 211 membranes tested over a range of temperatures.

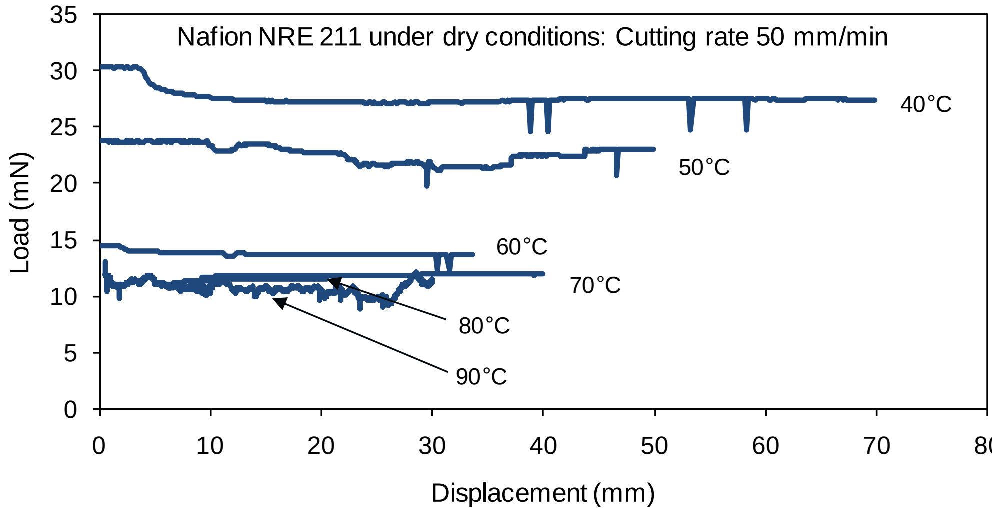

Figure 3. Typical load-displacement curve for Nafion NRE 211 specimen tested under dry conditions at various temperatures, at a cutting rate of 50 mm/min.

Overall, the load traces show that the forces recorded during the tests were relatively constant, except for a few regions where load drops were noted. The average force during cutting was calculated by ignoring the initial and ending regions of the load trace. The average force during each test was used to calculate the cutting, tearing and total slitting energies following equation 1. Figure 4 shows the fracture energy vs. the cutting rate, at different moisture levels and at representative temperatures of 60^{o}C and 80°C on a semi-logarithmic scale graph. It can be seen that the fracture energy drops with increase in temperature and relative humidity, and increases with increasing cutting rate.

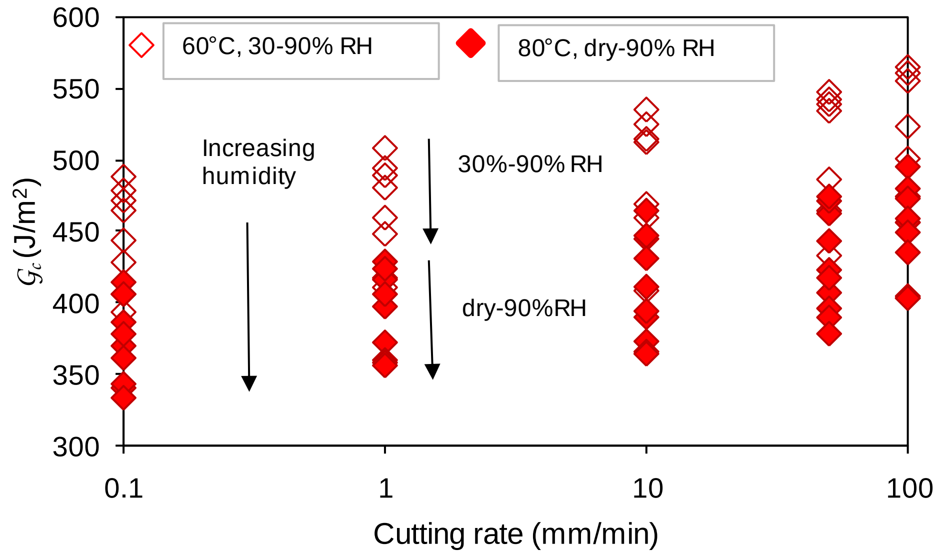

Figure 4. The fracture energy observed for Nafion® NRE 211 tested at 60°C and 80°C for various cutting rates and relative humidities (30-90% RH at 60°C and dry-90% RH at 80°C).

Polymers which are thermorheologically simple (TSM), follow the time-temperature superposition principle (TTSP). PEMs are even sensitive to moisture or humidity. We assume PEMs are hygrothermorheologically simple (HTSM) materials [7]. Thus they follow the principle of time temperature moisture superposition (TTMS) principle. Thus if a polymer is HTSM, then the viscoelastic quantity can be shifted using humidity shift factors (a_H) at constant temperature and subsequently can be shifted using temperature shift factors (a_T). It is often done in case of transient viscoelastic tests such as stress relaxation [7]. It is intriguing that the principle of MTTS is even applicable to the fracture energy of the PEMs, which suggests that the slitting process is viscoelastic in nature. Such doubly-shifted (humidity and temperature) master curves of fracture energy against rate of crack propagation are plotted in Figure 5 for Nafion NRE 211, Ion Power N111-IP, and GoreSelect 57 PEMs. Again, Nafion NRE211 membrane was characterized at various humidities, while N111-IP and GoreSelect 57 were characterized for fracture energy only under dry and 50% RH, as the tests were much quicker and still gave sufficient data to construct hygrothermal master curves for fracture energy with respect to reduced cutting rate. One should note that fracture and strength master curves often exhibit more scatter than is typical for master curves of constitutive data, which is often gathered in a more continuous fashion. The fracture energy at various temperatures and humidity conditions, seen as a function of cutting rate, seem to shift well. The principles of viscoelasticity dictate certain attributes to the process of the master curve construction. The master curve should be smooth, the shift factors reasonable, and the shift factors obtained from one viscoelastic process applicable to the other physical processes [8]. Figure 6 shows a comparison of the thermal shift factors obtained from stress relaxation and knife slitting process and Figure 7 shows the hygral shift factors measured. More information on transient viscoelastic characterization of these membranes can be found in papers by Patankar et al. [7, 9].

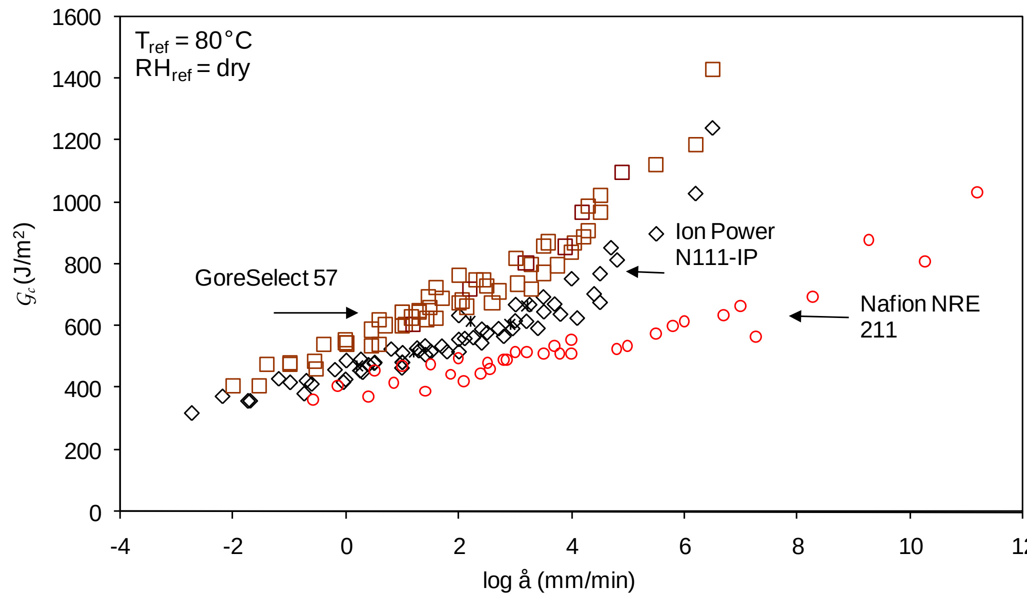

Figure 5. Comparison of master curves generated from shifting the fracture energy values at various temperature and humidity conditions for Nafion NRE 211, Ion Power N111-IP, and GoreSelect 57 membranes.

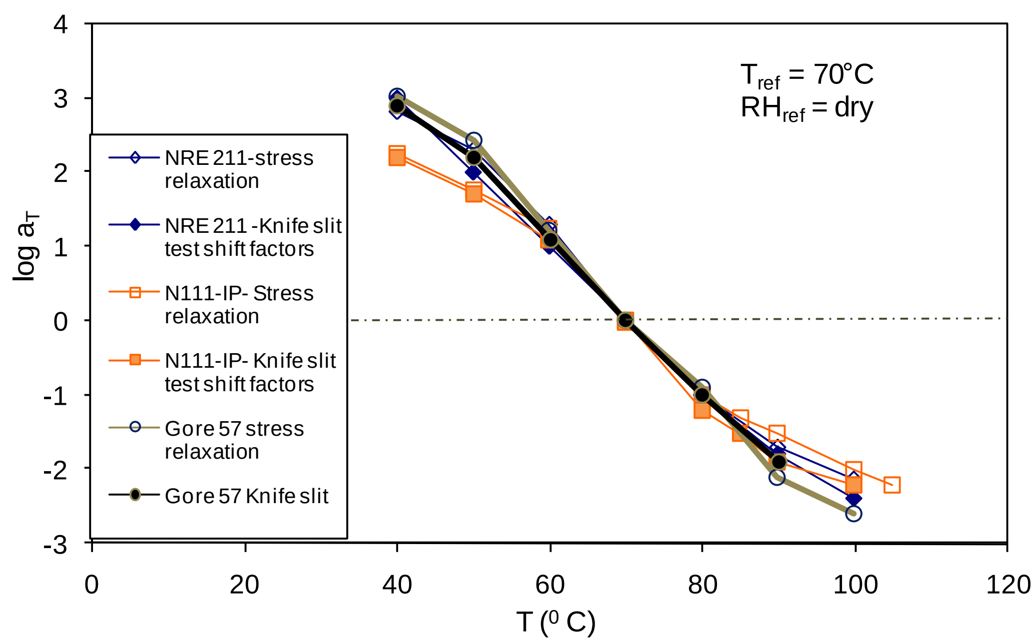

Figure 6. Comparison of temperature shift factors for Nafion NRE 211 and Ion Power N111-IP, and GoreSelect 57 obtained from stress relaxation and knife slitting tests.

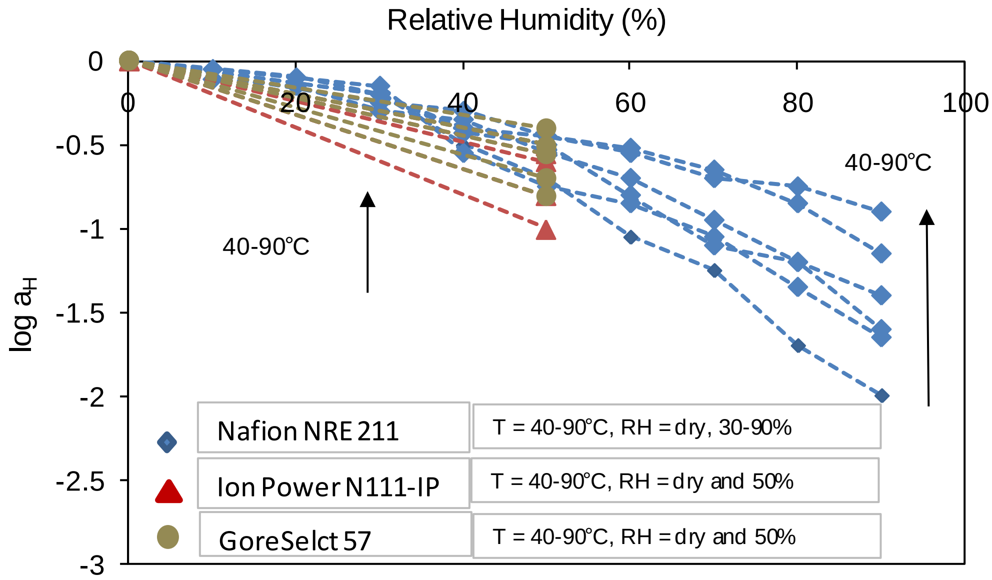

Figure 7. Comparison of hygral shift factors for Nafion NRE 211 and Ion Power N111-IP, and GoreSelect 57 obtained from the process of knife slitting.

It is also interesting to note the fracture energy seems to depend strongly on temperature, and rather weakly on humidity, as can be seen from the thermal and hygral shift factors. The total thermal shift from 40-90°C is about 5-6 decades, while the total hygral shift is about 1.5-2 decades (in case of Nafion NRE211). Also moisture seems to have lesser influence at higher temperatures. Thus in the temperature range that is most important to fuel cell operation (70-90°C), the fracture energy shows a strong dependence of temperature, but less dependence on relative humidity. The fracture energies obtained at the vanishingly slow reduced cutting rates (i.e. at high temperatures and humidity levels) may approach the intrinsic fracture energy of the membranes. A comparison of the master curves should provide information about their relative intrinsic fracture energy values. The three master curves seem to converge at the lowest reduced cutting rates, suggesting similar intrinsic cutting energies. Based on the limited data, we postulate that the three PEMs may have similar intrinsic fracture energy; however the fracture energy at higher rates is significantly different. Thus it can be seen that the fracture energy of both Ion Power N111-IP and GoreSelect 57 is 10-100% higher than that of Nafion NRE 211 at a given reduced cutting rate. The master curves have flatter slopes at lower reduced cutting rates, but have significantly different slopes (Gore Select 57 and Ion Power N111-IP being higher than Nafion NRE 211) at higher reduced cutting rates, cutting rates at a given value of fracture energy may be significantly different. For example, at a given fracture energy value, the reduced cutting rates associated with Nafion NRE211 and Ion Power N111-IP could differ as much as 2-4 decades. This suggests faster pinhole formation and propagation in NRE 211 as compared with N111-IP. This humidity cycling tests conducted at General Motors have corroborated this fact [10]. GoreSelect 57 appears to have the highest fracture toughness at a given cutting rate amongst the membranes tested. Perhaps this is not surprising as Gore Select 57 membrane is reinforced with expanded poly (tetrafluoroethylene) to enhance the mechanical properties.

Summary

The knife-slitting study initiated by Li et.al. was extended to several commercial proton exchange membranes in this study. Fracture tests were conducted to investigate the intrinsic fracture energy of Nafion NRE 211, N111-IP and GoreSelect 57 PEMs. Knowledge of this intrinsic fracture energy can help us understand the durability of PEM and MEA when subjected to creep and/or cyclic loading conditions where they may undergo slow cracking. The test fixture proved to be flexible and had the capability to perform knife-slit tests on thin membranes. Multiple tests under various temperature and humidity levels can be performed at different cutting rates on a single membrane specimen. To reduce the amount of membrane required to perform a test, the specimen was modified by attaching polyester leaders to the membrane Nafion NRE 211 and Ion Power N111-IP membranes were tested at various temperatures, humidities and cutting rates. The fact that the fracture energy still shows a rate-dependence suggests that viscous and plastic dissipation still played roles during the fracture process. Increasing the test temperature and lowering the cutting rate could further reduce viscous dissipation; better approximating the intrinsic fracture energy of the PEM. The fracture energy associated with the process was doubly shifted using temperature and humidity shift factors to construct the master curve. The ability to successfully shift the fracture energies with respect to temperature and humidity suggests that the slitting process is viscoelastic in nature. The master curves were then compared for the lowest measurable fracture energy and were found to collapse at low cutting rates. This may not be surprising as the polymers have the same chemical structure, and thus the process of slitting may be associated with the inherent chemical nature of the polymer. We believe the knife- slitting test can be used as a tool to differentiate between various PEMs based on the fracture energies measured at different rates.

Acknowledgment

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