

**ON NUMERICAL MODELING OF FATIGUE CRACK GROWTH
IN POLYMERS USING PLASTICALLY DISSIPATED ENERGY**

by

Guoliang Ding

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering

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ABSTRACT

Engineering structures are often subjected to repeated, cyclic loading rather than a simple static load. It is well established that cyclic loading results in progressive degradation and can lead to catastrophic failures of structures. In this case, the structure fails at load levels that are well below the load levels required to fail the structure under static loading, and is commonly referred to as *fatigue failures*. Fatigue failures are initiated by imperfections in the structure that develop into micro-cracks followed by slow and steady growing fatigue cracks, “Paris-regime” crack growth.

Predicting fatigue crack growth and fatigue life is an important part of preventing fatigue failure. Up to now, experimental characterization has been the only realistic method to predict fatigue life, but is usually expensive, time-consuming and not always reliable. This dissertation attempts to propose a method to minimize the time required for experimental characterization by investigating numerical modeling techniques of fatigue crack growth. In particular, this work explores the concept of using plastically dissipated energy as a criterion for fatigue crack growth.

At the continuum scale, fatigue crack growth is due to cyclic material degradation in a process zone ahead of the crack tip. For ductile materials, the degradation is associated with plastic deformation, and the plastically dissipated energy is directly linked to the net accumulation of the plastic strain during loadings. The premise of the proposed method is that once the accumulated plastically dissipated energy has reached a critical value, the crack will propagate incrementally. The plastically dissipated energy criterion has previously been successfully applied to

study Paris-regime crack growth for selected metals, utilizing the commercially available finite element program ABAQUS. This previous work also included a proposed method on how to establish the critical value of plastically dissipated energy. Here, the hypothesis and numerical scheme are adopted to study Paris-regime crack growth rate for a variety of polymers, including polymers whose Paris-regime crack growth behavior is *independent* of and those that is *dependent* on test frequency. Interestingly, the numerically predicted Paris-regime crack growth results are in good agreement with results obtained experimentally for both the frequency-independent and frequency-dependent polymers studied.

To demonstrate the versatility of a numerical scheme that predicts fatigue crack growth, the proposed method is applied to polymer electrolyte fuel cell membranes. In particular, the *in-situ* crack propagation in the membrane under relative humidity (RH) cycles is investigated. A two-dimensional representative volume element of a polymer electrolyte membrane fuel cell unit with a pre-existing crack is modeled. The model simulates a relative humidity (RH) protocol developed for testing the mechanical durability of the polymer electrolyte membrane. A range of well-established experimental observations are studied including crack propagation in unreinforced perfluorosulfonic acid (PFSA) membranes, and crack propagation in expanded polytetrafluoroethylene (ePTFE) reinforced PFSA membranes. The plastically dissipated energy criterion captures all of these observations qualitatively.

These analyses show that the plastically dissipated energy criterion can be used to estimate fatigue crack growth for a range of materials in a variety of engineering structures, and can therefore potentially reduce the cost to improve the reliability of engineering structures.

Chapter 1

INTRODUCTION

Engineering structures are generally used under repeated and cyclic loading conditions [1-7]. The repeated and cyclic loading, well below the load levels needed to fail the material under static loading, results in progressive degradation and can eventually lead to catastrophic failures of the material [1-7]. This phenomenon is commonly referred to as *fatigue failures* [1-7]. It has been estimated that 60% to 80% of the failures of mechanical components are associated with fatigue [8]. In order to prevent fatigue failure, extensive research has been conducted to develop methods and models to predict fatigue crack growth and fatigue life. Many experimental characterization models have been proposed, but conducting the experimental characterization is usually expensive and time-consuming. Numerical modeling using finite element analysis is a useful way to minimize the time and cost associated with experimental characterization, and this dissertation focuses on the application of plastically dissipated energy criterion in numerical modeling of fatigue crack growth.

1.1 Characterization of Fatigue Life

1.1.1 Experimental Characterization of Fatigue Life

Fatigue life is defined as the number of load cycles, N_f , that a specimen sustains before failure occurs [9] and is generally split into three phases: crack initiation, slow crack propagation and accelerated propagation to failure [10]. The crack initiation period consists of the nucleation of small defects into micro-cracks and

the subsequent growth or coalescence of the micro-cracks into dominating macro-cracks [10]. Manufacturing defects and other imperfections are the typical sources of the initial flaws. The slow crack propagation comprises a stable growth of the dominant macro-cracks into cracks of critical size [10]. Once the critical size of the cracks has been reached, an accelerated – typically unstable – crack propagation ensues, resulting in final failure [10].

Three main methods have been widely used to characterize the fatigue life of materials: the stress-life method, the strain-life method and the fracture mechanics method [11].

The stress-life method, proposed by Wöhler [12], is generally used to characterize high cycle fatigue, where the stress is low and the deformation is primarily elastic. In this case, the fatigue life is commonly characterized by an S-N curve, which is a graph of the magnitude of the stress amplitude S against the number of cycles to failure N (usually on a logarithmic scale). A typical S-N curve for this type of fatigue is shown in Figure 1-1 [4].

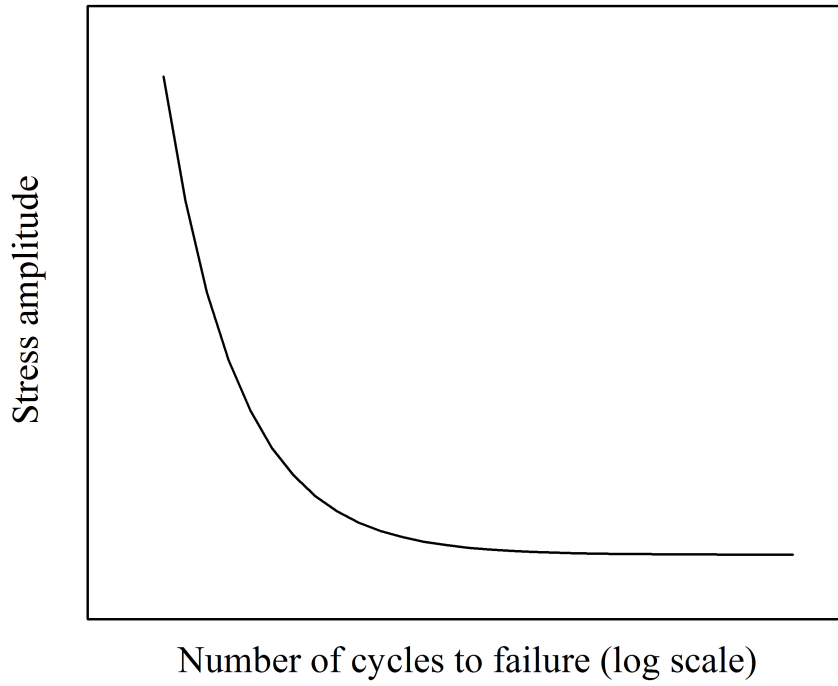


Figure 1-1 Typical S-N curve showing the variation of stress amplitude as a function of the number of cycles to failure for ferrous and nonferrous alloys [4].

The strain-life method, proposed independently by Coffin [13] and Manson [14], is used to characterize low-cycle fatigue, where the stress is high enough for plastic deformation to occur. The strain-life is generally characterized by the Coffin-Manson relation:

$$\frac{\Delta \epsilon_p}{2} = \epsilon'_f (2N)^c \quad (1.1)$$

where $\Delta \epsilon_p$ is the plastic strain amplitude, ϵ'_f is an empirical constant known as the fatigue ductility coefficient, $2N$ is the number of load reversals to failure and c is an

empirical constant known as the fatigue ductility exponent. A typical low-cycle fatigue curve ($\log \Delta \epsilon_p$ versus $\log 2N$) for metals is shown in Figure 1-2 [13].

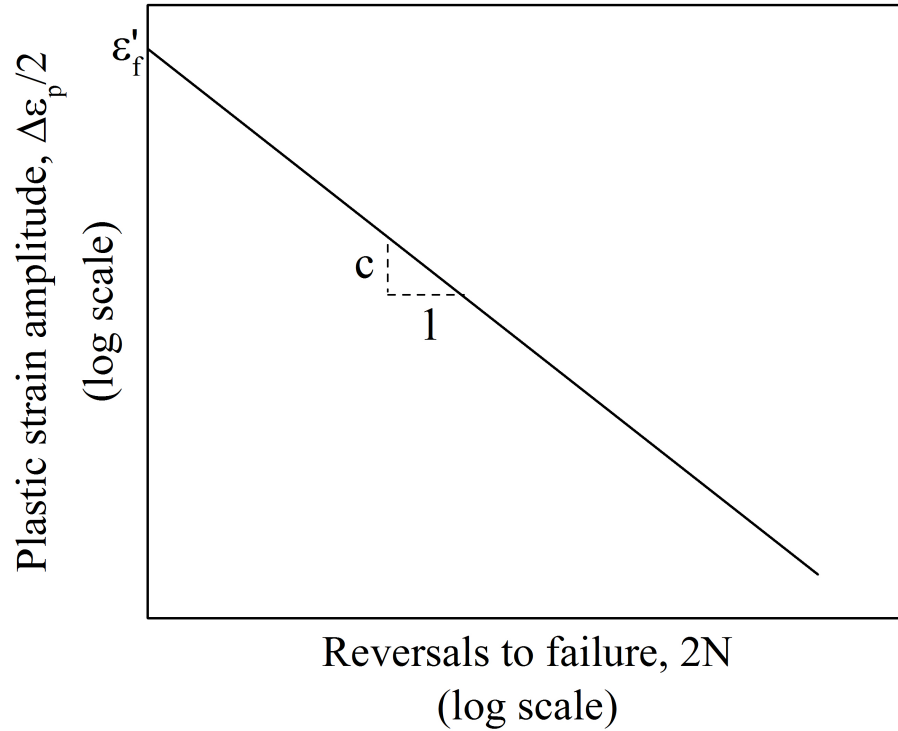


Figure 1-2 Typical low-cycle fatigue curve showing the variation of plastic strain amplitude as a function of the reversals to failure for metals [13].

The fracture mechanics method was pioneered by Paris and Erdogan [15] in the 1960s to use fracture mechanics concepts to characterize fatigue crack growth. The fundamental assumption is that similitude applies to the fatigue crack [16], i.e., that under certain conditions the crack tip can be uniquely defined by a single parameter

such as the stress intensity factor [16]. Figure 1-3 [16] shows a schematic plot of a typical fatigue crack growth behavior for many ductile materials in terms of crack growth rate, da/dN , versus range of stress intensity factor, ΔK .

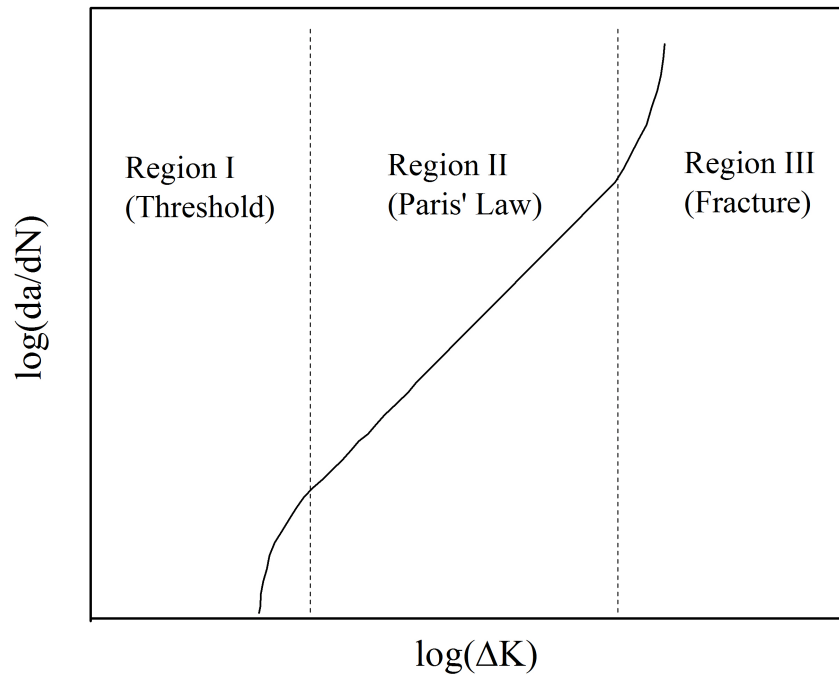


Figure 1-3 Typical fatigue crack growth behavior showing the crack growth rate as a function of the range of stress intensity factor for metals [16].

The curve contains three distinct regions with distinctly different fatigue crack growth behaviors. Region II is a region where there is a linear log-log relationship

between the fatigue crack growth rate da/dN and the range of stress intensity factor ΔK and is described by Paris' law [15] as:

$$\frac{da}{dN} = C\Delta K^m \quad (1.2)$$

where C and m are material parameters determined from experiments and are commonly called the *Paris coefficients*. “Paris law behavior” is widely accepted as an empirical description of fatigue crack growth in metals and a large number of experiments have been conducted to determine the Paris-regime crack growth curves and Paris coefficients for most structural metals [17,18].

These experimental characterization methods are very useful in life prediction and design assurance, but obtaining such experimental data requires detailed preparation of test specimens, long-time fatigue testing and precise measurement of the fatigue crack growth rate [19]. Moreover, the tests are done on standardized specimens that may or may not be a good interpretation of the real structural behavior. To reduce the time and cost required for conducting the fatigue experiments, as well as increasing the reliability of the life prediction models, physical modeling of fatigue crack propagation is appealing. Several useful methods have been proposed including damage mechanics [20-31] and energy criteria [19,32-44]. In this dissertation, the plastically dissipated energy criterion is investigated and extended for use in numerical simulation of fatigue crack growth in polymers.

1.1.2 Plastically Dissipated Energy Criterion

For ductile materials such as metals and polymers, plastic deformation develops at the crack tip during loading [32,45]. In metals, dislocation generation and motion, whereas shear banding and crazing in polymers, are associated with plastic

deformation, all of which are directly associated with fatigue [32,45,46]. Rice [32] first suggested the use of plastically dissipated energy as a criterion to study fatigue crack propagation. Since this early work, there have been analytical [33,34,36,39], experimental [35,38,42] and numerical [19,40,41,43,44] investigations into the application of plastically dissipated energy in predicting fatigue.

Following the work of Rice, and based on the assumption that the accumulated dissipative work in the plastic zone surrounding the crack tips controls the fatigue crack growth, Bonder et al. [36] suggested the decomposition of the crack growth rate da/dN as:

$$\frac{da}{dN} = \left(\frac{da}{dW_p} \right) \left(\frac{dW_p}{dN} \right) \quad (1.3)$$

where dW_p/dN is the non-recoverable work of plastic deformation per load cycle and da/dW_p is the ratio of an incremental increase in crack length to the corresponding non-recoverable work done on the cracked body.

Based on energy balance during a crack extension, Klingbeil [40] proposed an inverted form of the equation proposed by Bonder et al. [36].

$$\frac{dW}{dN} = \left(\frac{dW}{da} \right) \left(\frac{da}{dN} \right) \quad (1.4)$$

where dW/dN is the plastic work per load cycle and dW/da is the plastic work per unit crack extension. Klingbeil [40] further assumed that the plastic work per unit crack extension, dW/da , equaled the critical energy release rate G_c , so Equation 1.4 can be rewritten as:

$$\frac{da}{dN} = \left(\frac{1}{G_c} \right) \left(\frac{dW}{dN} \right) \quad (1.5)$$

The critical energy release rate G_c is a material property determined from experiment, values for which can be found in standard material handbooks [17,18]. Klingbeil [40] calculated the plastic dissipation per cycle, dW/dN , around the crack tip of a stationary crack under Mode I cyclic loading using finite element analysis, and the crack growth rate, da/dN , could then be determined using Equation (1.5). The numerically evaluated Paris-regime crack growth curve matched the experimental data fairly well for a variety of ductile metals. The method was later adopted by Daily and Klingbeil [41] to investigate fatigue crack growth under mixed-mode loading.

Cojocaru and Karlsson [43] proposed an alternate numerical approach based on plastically dissipated energy to predict the fatigue crack growth directly from finite element simulations. Cojocaru and Karlsson [43] suggested a crack growth criterion that compared the accumulation of plastically dissipated energy ahead of the crack tip with a critical value. The critical value of plastically dissipated energy was assumed to be a material property, analogous to the critical energy release rate. Once the accumulation exceeded the critical value of plastically dissipated energy, the crack was extended using a numerical node-release scheme. Therefore, the crack growth was simulated directly from the finite element simulations instead of being calculated using the plastically dissipated energy from a stationary crack as in Klingbeil [40]. With a two-dimensional plane strain model, Cojocaru and Karlsson [43] predicted changes in crack growth rates under negative load ratios and the effect of tensile overloads, and the results were in qualitative agreement with experimental observations. Using the same methodology as Cojocaru and Karlsson [43], Nittur et al. [19] extended the technique to study Paris-regime crack growth. In Nittur et al. [19], the critical value of plastically dissipated energy was obtained from a single

experimental (ΔK , da/dN) data point. Once the critical value of plastically dissipated energy was established, the crack growth rate for different levels of ΔK could be obtained directly from finite element simulations using the plastically dissipated energy criterion with a node-release scheme. Using this technique, Nittur et al. [19] were able to produce a very good match between the numerically predicted and the experimentally measured Paris-regime crack growth for a variety of ductile metals.

Modification and extension of the numerical technique proposed in Cojocaru and Karlsson [43] and augmented in Nittur et al. [19] is applied in this work to extend the applicability of the plastically dissipated energy to simulate a range of crack growth responses in polymers. A brief description of the numerical scheme proposed in Cojocaru and Karlsson [43] and augmented in Nittur et al. [19] is presented in the following section.

1.1.3 Numerical Framework to Predict Crack Growth Rate

The numerical framework to predict crack growth rate using plastically dissipated energy is based on a node-release scheme. The node-release scheme simulates crack growth by releasing previously tied nodes ahead of the crack tip when a propagation criterion is fulfilled.

The plastically dissipated energy over the loading history in a region, can be calculated by:

$$W^p = \iiint \sigma_{ij} d\varepsilon_{ij}^p dV \quad (1.6)$$

In finite element analysis, the integration is performed over the volume V of each element in the region of integration and W^p is the plastically dissipated energy within the region over the loading history. The commercially available finite element

software ABAQUS calculates the plastically dissipated energy within each element during each loading step and these values can be extracted from the solver output at each step.

For the numerical implementation, the plastically dissipated energy is evaluated in a fixed-volume region at the current crack tip, denoted as the dissipation domain. This dissipation domain is associated with the crack tip and will travel with it as the crack propagates. Because of the discrete nature of finite element analysis, the dissipation domain is most conveniently chosen as a set of elements. The total plastically dissipated energy of the dissipation domain can be calculated by summing the plastically dissipated energy of all the elements that are within the dissipation domain. Nittur et al. [19] suggested the dissipation domain should be a rectangular domain that completely encloses the reverse yielding zone ahead of the crack tip.

As a demonstration of the method, consider the beginning of the cycle N_t (the end of the cycle N_{t-1}), and assume the crack has just propagated to a new tip T_t and the dissipation domain associated with the crack tip is D_t . The accumulation of the plastically dissipated energy within the dissipation domain D_t during this loading cycle N_t , $\Delta W^p(D_t | N_t)$, is calculated as the difference between the plastically dissipated energy at the end of the loading cycle N_t and that at the beginning. Since the crack has just propagated to the new tip, the total accumulation of plastically dissipated energy, ΔW^p , associated with the crack tip location T_t and dissipation domain D_t is tracked from this point to predict the next increment of growth as:

$$\Delta W^p = \Delta W^p(D_t | N_t) \quad (1.7)$$

where $(D_l|N_l)$ means in dissipation domain D_l and during loading cycle N_l . The total accumulation of plastically dissipated energy ΔW^p is compared to the critical value of plastically dissipated energy, W_{cr}^p , which is assumed to be a material property.

If $\Delta W^p < W_{cr}^p$, the next loading cycle N_{t+1} is applied. The total accumulation of plastically dissipated energy ΔW^p at the end of loading cycle N_{t+1} is:

$$\Delta W^p = \Delta W^p(D_1 | N_t) + \Delta W^p(D_1 | N_{t+1}) \quad (1.8)$$

Then the comparison is conducted again with the critical value of plastically dissipated energy.

If $\Delta W^p \geq W_{cr}^p$, the crack propagates by the length of one element ahead of the tip using a node-release scheme. A new crack tip T_2 is formed and a new dissipation domain D_2 is associated with the new crack tip T_2 , so the total accumulation of plastically dissipated energy ΔW^p associated with the new crack tip location T_2 (dissipation domain D_2) now is:

$$\Delta W^p = \Delta W^p(D_2 | N_t) \quad (1.9)$$

Then the comparison with the critical value of plastically dissipated energy is conducted again.

A discrete crack propagation rate $\Delta a/\Delta N$ can be directly obtained from this simulation and can be considered a discrete equivalent of the continuous crack propagation rate da/dN over the crack extension length [19,43].

In this dissertation, the plastically dissipated energy criterion is first adopted to study Paris-regime crack growth in polymers. After verifying its applicability in studying fatigue crack growth in polymers, the methodology is extended to study mechanical degradation of polymer electrolyte membranes by investigating the crack

growth in the membranes under relative humidity cycling. Finally, the mechanical degradation of polymer electrolyte membranes is briefly introduced.

1.2 Mechanical Degradation of Polymer Electrolyte Membrane

1.2.1 Polymer Electrolyte Membrane Fuel Cell

A fuel cell is an electrochemical device that converts chemical energy into electrical energy [47]. The need for clean power with higher efficiency has drawn great interest in fuel cell technology because fuel cells can reach an overall efficiency of 50%, and their byproducts are just water and heat if hydrogen and air are used as reactants [47].

Several fuel cell systems have been developed and each different type has its own advantages, limitations and applications [48]. Among these different kinds of fuel cells, this work focuses on polymer electrolyte membrane (PEM) fuel cells. PEM fuel cells offer many advantages over the other types because of their relatively low operating temperature, high energy density, quick start-up, flexible scale-up capability and high efficiency [49]. Because of these features, PEM fuel cells have promising applications ranging from portable power sources to large-scale stationary power systems for buildings [49]. In particular, the automotive industry is interested in replacing traditional combustion engines with PEM fuel cell stacks as power sources because the efficiency of traditional combustion engines is limited by the Carnot cycle and their byproducts have caused serious environmental problems worldwide [49]. In 2014, Hyundai introduced the Tucson[®] fuel cell vehicle. In 2015, Toyota introduced to market its fuel cell vehicle Mirai[®]. In March 2016 Honda launched its fuel cell vehicle Clarity[®].

A schematic representation of the polymer electrolyte membrane (PEM) fuel cell system at different levels is shown in Figure 1-4. A single PEM fuel cell contains a polymer electrolyte membrane, which serves to conduct protons from the anode to the cathode while insulating against electron flow and preventing the crossover of reactant gases [50]. Usually, the membrane is coated with porous carbon supporting platinum (Pt) particles serving as both catalyst and electrode [50]. The membrane and electrode together form the membrane electrode assembly (MEA), which is sandwiched between gas diffusion layers (GDLs). The GDL is usually made of porous carbon paper, which helps the reactants to diffuse to the active area of the membrane to increase active reacting surface area [51]. It also helps diffuse the by-product water generated by the reaction away from the active area of the membrane to maintain the proper moisture level in the fuel cell system [51]. The MEA and GDLs are then clamped between bipolar plates. The bipolar plates are usually made of graphite or stainless steel and help with conduction of electrical current, removal of heat generated during fuel cell operation and prevention of leakage of gases [52].

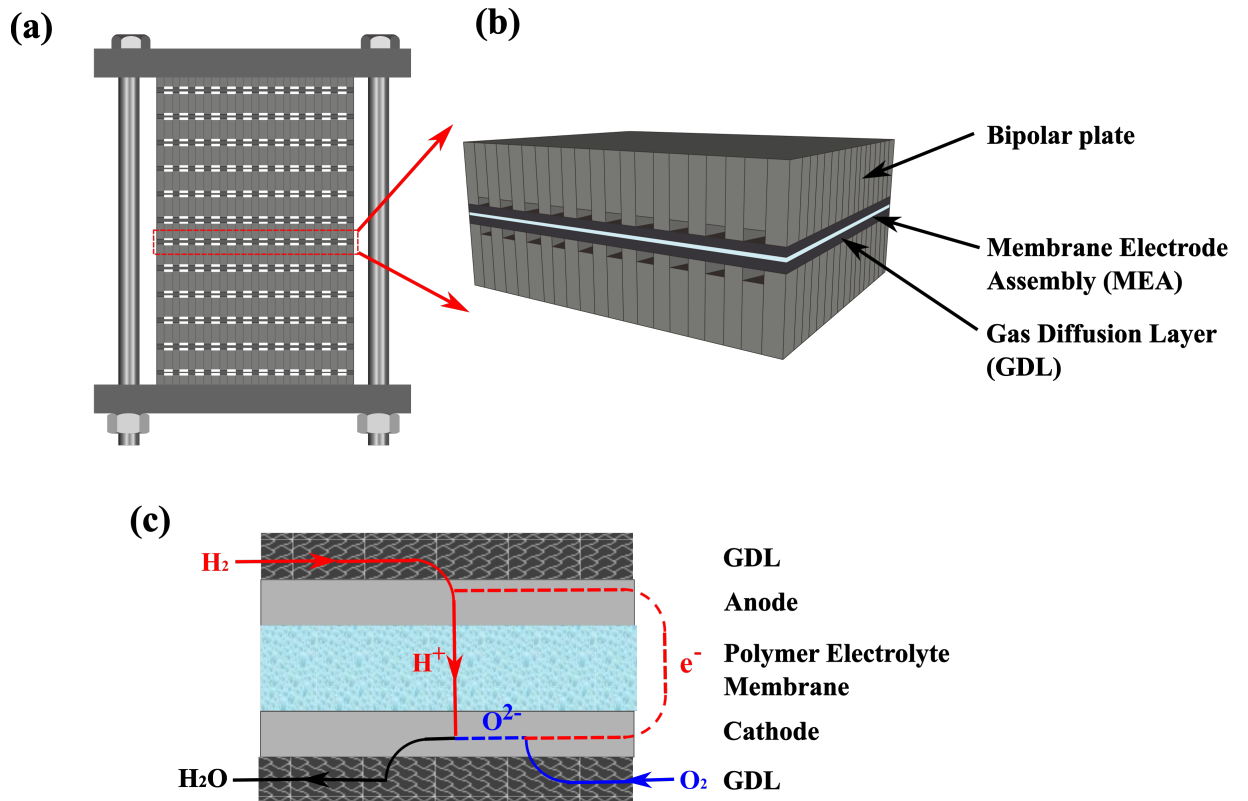


Figure 1-4 Schematic of PEM fuel cell at different levels: (a) a fuel cell stack; (b) a single fuel cell unit; (c) fuel cell operation in MEA. [53,54]

The U.S. Department of Engineering (DoE)/Federal Transit Administration (FTA) sets an ultimate performance target of 12 years/500,000 miles durability for the polymer electrolyte membrane (PEM) fuel cell propulsion system [55]. In order to reach this lifetime requirement to be competitive with internal combustion engines and achieve widespread commercialization, a clear understanding of the factors that affect the operating lifetime of the PEM fuel cell system needs to be established. However, understanding the degradation mechanism of the PEM fuel cell system is challenging as the system contains a wide range of components and failure in any one of the components may lead to the failure of the whole PEM fuel cell system [56]. Among

the components, the durability of the polymer electrolyte membrane is of crucial importance and it is the focus of this work.

1.2.2 Polymer Electrolyte Membranes and their Mechanical Degradation

Perfluorosulfonic acid (PFSA) ionomer is the most commonly used electrolyte materials in polymer electrolyte membrane fuel cell technology. The Nafion^{®*} membrane developed by DuPont in the 1970s is the benchmark product among commercially available PFSA membranes [57].

Failure of polymer electrolyte membranes is signaled by increased crossover of reactant gases from through-thickness cracks or pinholes which are formed by a combination of chemical and mechanical degradation during fuel cell operation [56,58-61]. The initiation and propagation of cracks in polymer electrolyte membranes is not yet fully understood but it is generally considered to be caused by a combination of environmental operational factors, such as hygrothermally induced mechanical stress [56,58,60,62]. Other typical failure drivers include: chemical degradation caused by attack from peroxide and hydroperoxide radicals produced from the side reactions during cell operation, defects from the membrane manufacturing process or membrane electrode assembly (MEA) fabrication process, and thermal degradation due to operating temperature around the glass transition temperatures of the perfluorosulfonic acid (PFSA) polymers [60,62]. However, the actual failure mechanisms in the cell are complex since a combination of chemical, mechanical and even thermal stressors results in synergistic effects accelerating the degradation [56,59,61,63-65]. One such synergetic effect is the chemical decomposition of ionomer causing local defects,

* Nafion[®] is a registered trademark of E.I. DuPont De Nemours & Co.

which act as crack-initiation sites and could grow under mechanical stresses, leading to enhanced crossover and higher rates of chemical decomposition. Moreover, it has recently been shown that the defect growth is a good metric to monitor the membrane's lifetime and fatigue behavior since there exists a correlation between the gas crossover and defect size in membranes [66,67]. Thus, investigation of crack-growth mechanisms due to mechanical stresses during relative humidity (RH) cycling is of great interest for elucidating the factors controlling chemical/mechanical durability and developing strategies for improved membrane stability.

Mechanical stresses are associated with swelling and shrinkage of the membrane as a result of environmental changes inside the cell during operation. Hydration and heating lead to hygrothermal swelling strains in the membrane [68-71]. However, the membrane is generally constrained in the fuel cell system by gas diffusion layers (GDLs), bipolar plates and gaskets, preventing the membrane from expanding. Consequently, significant compressive stresses can develop with increased temperature and swelling. The stresses developed from humidity cycling frequently exceed the elastic limit of the membrane, resulting in permanent deformation of the membrane during swelling and residual tensile stresses during shrinking [68-71]. In these cases, the membrane is subjected to cyclical compressive and tensile stresses (i.e. fatigue) during the cyclical hydration-dehydration and heating-cooling occurring during fuel cell operation [68-71]. Thus, with the combination of the cyclic fatigue loading and the environmental factors, microcracks can easily initiate and grow into through-thickness cracks, increasing the gas crossover through the membrane and causing the eventual catastrophic failure of the polymer electrolyte membrane (PEM) fuel cells [59].

To characterize the mechanical degradation of PFSA membranes, constitutive models have been developed by a number of researchers to describe the mechanical behavior of the membranes under varying temperatures, relative humidity (RH) and strain rates through different experimental techniques including dynamic mechanical analysis (DMA), uniaxial tensile, stress relaxation and creep [58,72-75]. Tang et al. [72] used isotropic linear elastic behavior to model the membrane along with isotropic thermal expansion and swelling, and measured the modulus and swelling coefficients as functions of temperature and RH. Kusoglu et al. [68] extended this model to include linear elastic perfectly-plastic behavior and modeled swelling as a polynomial function of temperature and hydration levels. This extension required the evaluation of the proportional limit as a function of temperature and RH. Kusoglu et al. [69] further improved the model including isotropic hardening beyond the proportional limit. To account for the time-dependent behavior of the membrane, Lai et al. [58] modeled the membrane as a linear viscoelastic material with linear thermal expansion and swelling. Khattra et al. [76] proposed a two-layer viscoelastic-plastic model that captured the strain-rate dependence of the instantaneous modulus. These models were then incorporated into finite element programs to calculate the distribution of the stress inside the membrane during simulated fuel cell operations as a function of temperature, RH and strain rate [68-70,76]. Based on the predicted stress distribution, regions of the membrane that are more likely to fail as a result of mechanical degradation were identified [71].

These studies laid the foundation to investigate the mechanical degradation of PFSA membranes, and *ex-situ* and *in-situ* characterization of the mechanical degradation of PFSA membranes has been the subject of a series of investigation in

recent years. The overall goal has been to create a model capable of predicting the failure of the membranes due to crack initiation and propagation or pin-hole formation, and eventually predict the lifetime of the membranes under mechanical degradation [77].

1.2.3 *Ex-situ* Characterization and Modeling

Dillard and coworkers [78-82] conducted a series of *ex-situ* experiments to characterize the fatigue and fracture properties of PFSA membranes. Li et al. [79] investigated the *ex-situ* fatigue response of commercially available polymer electrolyte membranes using pressure-loaded blisters. The use of the blister test induced an equal biaxial stress state within the central region of the pressured blister, which simulates the biaxial stress state in polymer electrolyte membranes during fuel cell operations. Typical fatigue lifetime curves that consist of a crack-formation dominated zone at high stress levels and a crack-propagation dominated zone at low stress levels were constructed. Li et al. [79] found that in the crack-formation dominated zone, cyclic stresses decrease faster than that in the propagation-dominated zone, and Li et al. [79] attributed this to crack/craze formation. Pestrak et al. [81] extended the application of fatigue testing of pressure-loaded blisters to study the lifetimes of membrane electrode assemblies (MEAs). Pestrak et al. [81] found that in untested MEAs there were no membrane cracks associated with the mud-cracks in the electrodes (cracks in the unused catalyst layers due to the manufacturing process and/or handling), while in tested MEAs there were membrane cracks associated with the mud-cracks. These finding suggested that mud-cracks in electrodes act as stress concentration sites and lead to crack initiation and subsequent crack propagation in the membrane.

Aindow and O'Neill [83] adapted an *ex-situ* mechanical fatigue life analysis used for lifetime prediction in structural materials to characterize polymer electrolyte membranes. The samples were prepared in dog-bone geometry and cyclically loaded in a dynamic mechanical analysis (DMA) machine equipped with an environmental chamber at constant 60°C and 90% relative humidity (RH) but under various stress amplitudes. The results were used to construct the S-N curves for fatigue lifetime prediction. Then the mechanical stress induced by a change in relative humidity (ΔRH) was measured using a fixed strain test. With these two curves (S-N and S- ΔRH) established, the S-N curves measured from cyclic mechanical stress testing were converted to ΔRH versus cycles-to-failure (ΔRH -N) curves.

Khorasany et al. [84] proposed a similar *ex-situ* fatigue test of polymer electrolyte membranes to characterize the effect of mechanical cyclic loadings on the fatigue lifetime of the membrane under a range of environmental conditions. The membrane specimens were also prepared in dog-bone shapes and loaded using a DMA machine, but under different combinations of temperature and relative humidity (RH) conditions. Measured fatigue lifetime curves in the form of S-N curves were constructed for the membrane under different conditions. Khorasany et al. [84] found that the membrane fatigue life increased exponentially with reduced stresses under all the environmental conditions tested. Increased temperature or RH both decreased the fatigue life, and the effect of temperature was found to have a more significant effect. Khorasany et al. [85] later suggested a numerical scheme using the Smith-Watson-Topper (SWT) [86] approach to model the *ex-situ* fatigue response of the membrane under mechanical cyclic loading. The proposed numerical scheme was then used to

investigate the fatigue of the membrane under combined *ex-situ* mechanical and hygrothermal cyclic loading.

These *ex-situ* characterization and modeling efforts, in the form of stress or change of relative humidity (RH) versus cycles-to-failure curves, show the fatigue behavior of the polymer electrolyte membrane, but offer no insight into the degradation process and ignore the *in-situ* effects of the other fuel cell components [71,77]. To overcome these shortcomings, *in-situ* characterization is needed to supplement *ex-situ* characterization.

1.2.4 *In-situ* Characterization and Modeling

A common *in-situ* test to investigate the fatigue properties and mechanical durability of the membrane is the accelerated stress test, which subjects the full cell to relative humidity (RH) cycling [59]. In the test, the polymer electrolyte membrane (PEM) fuel cell is exposed to inlet gases that change rapidly from low and high RH at 80 °C in the absence of electric potential [59]. Lai et al. [87] investigated the failure modes and crack morphology of membrane samples after RH cycling tests using cross-sectional micrographs. Figure 1-5, reprinted from Lai et al. [87], shows micrographs of three polymer electrolyte membranes removed from a cell after undergoing humidity cycling. A wide range of crack lengths was seen in each failed membrane sample, implying that the cracks in the membrane grew gradually instead of catastrophically. Transverse cracks extended from the electrodes into the membrane, suggesting that the cracks initiate in the electrodes and then propagate through the membrane during RH cycling.

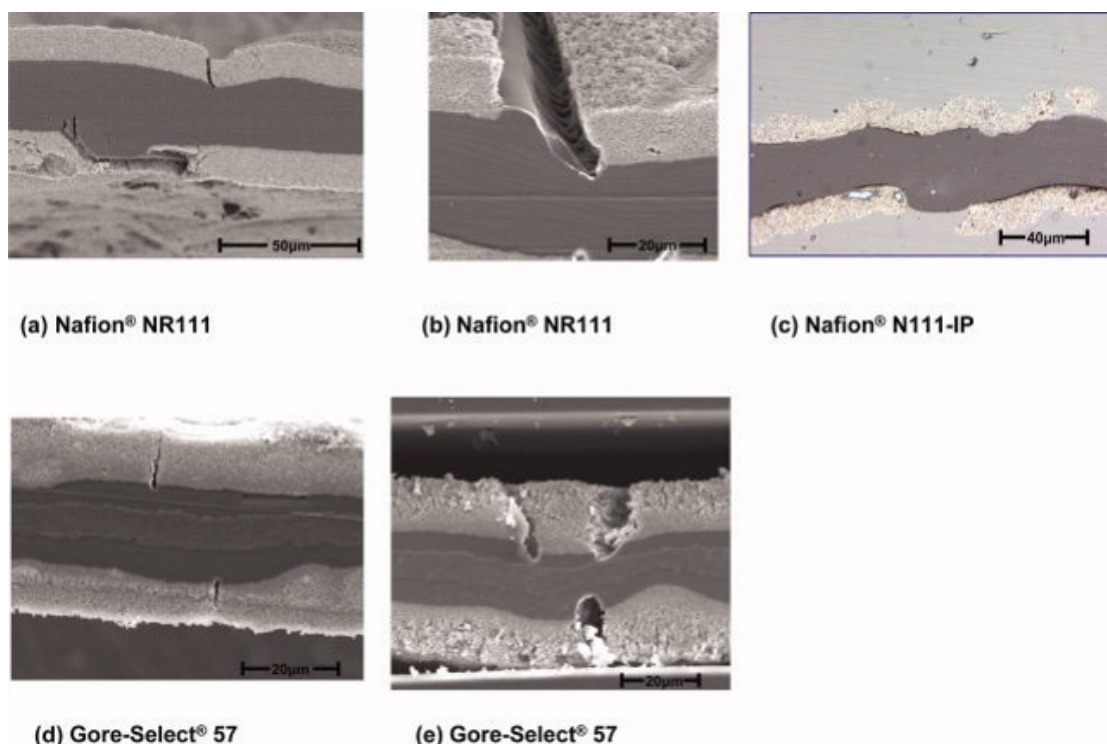


Figure 1-5 Representative postmortem cross-sectional micrographs of the three commercially available PFSA membrane (a) Nafion[®] NR-111 membrane, (b) Nafion[®] NR-111 membrane (c) Nafion[®] N111-IP membrane (d) Gore-Select^{®†} 57 membrane and (e) Gore-Select[®] 57 membrane [87] (Reprinted with permission from Wiley Books).

Burlatsky et al. [88] suggested a mathematical modeling framework to predict the lifetime of polymer electrolyte membranes subjected to hydration cycling. The modeling framework consists of three model components: The first model component calculates the relative humidity (RH) distribution in the gas channels as a function of the operation conditions and time. The second model component predicts the stress profile given the RH profile. The third model component predicts the lifetime of the

[†] Gore-Select[®] is a registered trademark of W.L. Gore Inc.

membrane using the damage accrual model by relating to experimental data for membrane failure under cyclic stress. With these three models, Burlatsky et al. [88] predicted the membrane lifetime (the number of cycles to failure) as a function of minimum RH at the cathode side of the membrane (the anode side of the membrane was held at 100% RH).

Banan et al. [89] recently developed a cohesive zone model for *in-situ* crack growth in a PEM fuel cell under relative humidity (RH) cycling. The effects of RH cycle amplitude, RH distribution profile, location of the defect and gas flow channel alignment were investigated. However, instead of modeling the crack growth through the thickness direction, which is the more general case observed in PEM fuel cell testing, Banan et al. [89] modeled crack growth in the in-plane direction. What's more, linear elastic-plastic material properties were applied in developing the model and the viscoelasticity of the membrane was not considered. Khattra et al. [76] showed that models using the time-dependent membrane properties predicted larger peak compressive and residual tensile stresses in the membrane than those using time-independent properties during hygrothermal load. Thus, the inclusion of the time-dependent material properties would likely predict different damage propagation in the cohesive zone model.

To the author's knowledge, no attempt has been made to model *in-situ* crack-propagation in a polymer electrolyte membrane during cyclical hygrothermal loading, using time-dependent visco-plastic membrane mechanical properties. In this dissertation, *in-situ* crack propagation in a polymer electrolyte membrane under RH cycling is investigated using finite elements analysis and the plastically dissipated energy criterion.

1.3 Objective and Outline

The research presented in this dissertation aims at extending the plastically dissipated energy criterion to study fatigue crack propagation in polymers in general and in polymer electrolyte fuel cell membranes in particular.

Chapter 2 focuses on the numerical evaluation of Paris-regime crack propagation in polymers. The numerical approaches proposed in Klingbeil [40] and in Nittur et al. [19] are combined to study the Paris-regime crack growth of polymers using plastically dissipated energy. The crack growth rate is calculated as the accumulation rate of plastically dissipated energy divided by the critical value of plastically dissipated energy per incremental increase in crack length. The accumulation rate of plastically dissipated energy is obtained from a two-dimensional finite element model of a standard compact tension specimen, while the critical value of plastically dissipated energy is assumed to be a material property and is determined using the method proposed in Nittur et al. [19]. Paris-regime curves are constructed and compared to experimental data. Two classes of polymers are investigated: those exhibiting frequency-*independent* fatigue crack growth and those exhibiting frequency-*dependent* fatigue crack growth.

Chapter 3 focuses on the application of the plastically dissipated energy in studying crack propagation in polymer electrolyte fuel cell membranes under cyclic relative humidity (RH) cycling. Two-dimensional plane strain models are created for representative unit volumes of a PEM fuel cell using the commercial finite element package ABAQUS. A range of well-established experimental observations are studied including crack propagation in unreinforced perfluorosulfonic acid (PFSA) membranes, crack propagation in expanded polytetrafluoroethylene (ePTFE) reinforced PFSA membranes, the differences between crack propagation under the

channel and land regions in a typical flow channel architecture, the effect of fuel cell clamping pressure on membrane cracking as well as the effect of different humidity cycling profiles on number of cycles to failure under RH cycling tests.

Chapter 4 focuses on determining the critical value of plastically dissipated energy for unreinforced PFSA. *Ex-situ* mechanical fatigue tests are conducted on pre-cracked rectangular Nafion[®] 211 specimens in an MTS[®] 858 Mini Bionix[®] II material testing system with an ESPEC[®] environmental chamber. The numbers of cycles to failure are recorded for different combinations of temperatures, relative humidity (RH) and mean loads. Then, finite element simulations are used in an attempt to determine the critical value of plastically dissipated energy by matching the simulation results with the experimental results.

Chapter 2

NUMERICAL EVALUATION OF PARIS-REGIME FATIGUE CRACK GROWTH IN POLYMERS BASED ON PLASTICALLY DISSIPATED ENERGY

2.1 Introduction

Paris-Law behavior, a linear log-log relationship between crack growth rate da/dN and stress intensity factor range ΔK (refer to Section 1.1.1 on the fracture mechanics method for detailed discussion), is widely accepted as an empirical description of fatigue crack growth in metals and a large number of experiments have been conducted to determine Paris-regime crack growth curves and Paris coefficients for most structural metals [17,18]. Some polymers also exhibit Paris-regime behavior and the influence of loading frequency on the crack growth rate has been investigated [90-101]. Polymers such as Polycarbonate (PC) [93,97,98,101] and Nylon 66 [94,98,100,101] exhibit little change in Paris-regime crack growth behavior as load frequency changes, while others, such as poly-methyl-methacrylate (PMMA) [90,92,98,101], polystyrene (PS) [96,98,99,101] and poly-vinyl-chloride (PVC) [91,95,98,101], show a significant increase in fatigue resistance (decrease in fatigue crack growth rate) as loading frequency increases.

Nittur et al. [19] extended the plastically dissipated energy criterion proposed by Cojocaru and Karlsson [43] to study Paris-regime crack growth. With the plastically dissipated energy criterion and node-release scheme, Nittur et al. [19] were

able to produce a very good match between the numerically predicted and the experimentally measured Paris-regime crack growth for a variety of ductile metals.

In this chapter, the approach used in Nittur et al. [19] is combined with the methodology proposed in Klingbeil [40] to study the Paris-regime crack growth of polymers using the plastically dissipated energy criterion. The numerical predictions are compared with experimental Paris-regime crack growth rate data for a variety of polymers, including PC and Nylon 66, whose Paris-regime crack growth behavior is independent of loading frequency, and PS, PVC and PMMA, whose behavior is dependent on loading frequency.

2.2 Numerical Framework

2.2.1 General Concepts

To formulate a predictive algorithm, the approaches proposed in Klingbeil [40] and in Nittur et al. [19] are combined, and it is assumed that the crack growth rate da/dN can be expressed as:

$$\frac{da}{dN} = \frac{dW_p/dN}{(dW_p/da)_{cr}} \quad (2.1)$$

where dW_p/dN is the accumulation rate of plastically dissipated energy, determined from numerical simulations, and $(dW_p/da)_{cr}$ is the critical value of plastically dissipated energy required per incremental increase in crack length, which is assumed to be a material property.

During cyclic loading, when a cracked body is first loaded in tension, a plastic zone is formed as the material ahead of the crack tip yields in tension (Figure 2-1) (the forward plastic zone) [32]. During the unloading phase, a smaller zone is typically

formed within the forward plastic zone as the material yields again, this time in compression (the reverse plastic zone) [32]. As the crack propagates, this zone of yielded material grows behind the advancing tip, leaving behind a region of yielded material called the plastic wake [19]. In the work of Nittur et al. [19], the crack was manually propagated through the initial reverse plastic zone formed at the end of the first cycle, without considering the crack-growth criterion. This procedure ensures that a fully developed plastic wake has formed [19]. After that, the accumulation of plastically dissipated energy is tracked and compared to the critical value of plastically dissipated energy to determine further crack propagation [19]. In this work, the same procedure is adopted to form a fully developed plastic wake. Then the accumulation rate of plastically dissipated energy, dW_p/dN , is calculated and used in Equation (2.1) to predict the crack growth rate.

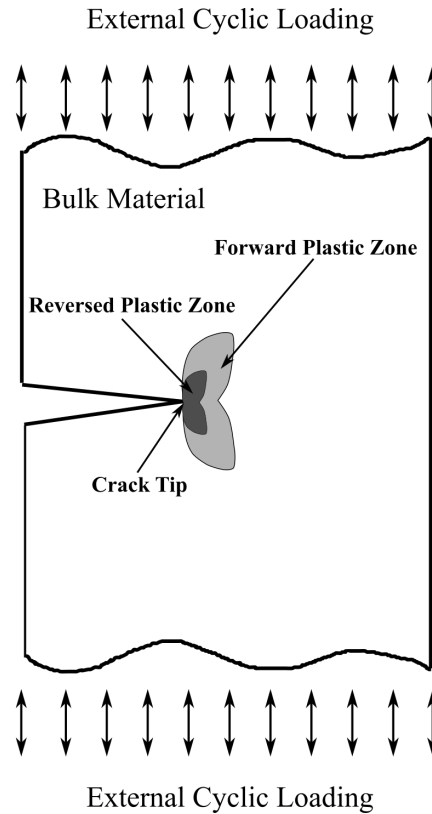


Figure 2-1 Forward and reverse plastic zones developed during cyclic loading around a crack tip (size and shape not to scale) [19,43].

The finite element platform used here, ABAQUS [102], calculates the plastically dissipated energy for each plastically deforming element during each load step as part of the analysis, so the accumulation of plastically dissipated energy for a given element can be taken directly from the finite element simulation results. To calculate dW_p/dN for a particular region, the change of plastically dissipated energy is obtained by summing the accumulation of plastically dissipated energy in each element within the region and then averaging over the number of cycles. Nittur et al. [19] suggested that a suitable region in which to monitor the accumulation of plastically dissipated energy is a rectangular region that fully encloses the initial

reverse plastic zone formed at the end of the first loading cycle, and a similar region is used in this study.

2.2.2 The Critical Value of Plastically Dissipated Energy $(dW_p/da)_{cr}$

In this work, it is assumed that the accumulation of plastically dissipated energy is directly linked to the non-elastic degradation at the crack tip which leads to crack propagation. No matter what the strain rate is, the crack is assumed to propagate incrementally once the accumulation of plastically dissipated energy reaches a critical value. Therefore, the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is assumed to be a material property that is independent of strain rate. To the knowledge of the authors, there is no experimental data available in the open literature on $(dW_p/da)_{cr}$. The term $(dW_p/da)_{cr}$ used here is similar to the critical plastically dissipated energy, W_{cr}^p , introduced in Nittur et al. [19]. In Nittur et al. [19], W_{cr}^p is determined by matching one simulation data point $(\Delta K, \Delta a/\Delta N)$ with one experimental data point $(\Delta K, da/dN)$. In this work, the procedure is adapted to determine $(dW_p/da)_{cr}$ by matching one simulation data point $(\Delta K, dW_p/dN)$ with one experimental data point $(\Delta K, da/dN)$.

For a selected ΔK , the crack growth rate, da/dN , can be obtained from experimental data. The corresponding accumulation rate of plastically dissipated energy at the selected ΔK , dW_p/dN , can then be determined via simulations using the finite element model described in Section 2.3. Given dW_p/dN , the value of $(dW_p/da)_{cr}$ that results in the experimentally obtained da/dN is used as the actual value of $(dW_p/da)_{cr}$. Therefore, with one experimental data point $(\Delta K, da/dN)_{exp}$ and the corresponding simulation data point $(\Delta K, dW_p/dN)_{sim}$, $(dW_p/da)_{cr}$ can be calculated from an inverted form of Equation (2.1) as:

$$(dW_p/da)_{cr} = \frac{(dW_p/dN)_{sim}}{(da/dN)_{exp}} \quad (2.2)$$

Since it is considered to be a material property, the value of $(dW_p/da)_{cr}$ determined at the selected ΔK level will be used in other ΔK levels to calculate the corresponding crack growth rate using Equation (2.1). The influence of the choice of the experimental data point (ΔK , da/dN) to determine $(dW_p/da)_{cr}$ on the results will be discussed in Section 2.4.1.3

2.2.3 Comparison with the Methods in Klingbeil [40] and Nittur et al. [19]

In this work, the approaches proposed in Klingbeil [40] and in Nittur et al. [19] are combined to formulate a numerical scheme to predict Paris-regime crack growth in polymers. The fundamental assumption is the same as that in Klingbeil [40] and in Nittur et al. [19], which relates the crack growth to the plastically dissipated energy at the crack tip. However, there are some distinct differences.

The first difference from Klingbeil [40] is that in that work, the plastic work per unit crack extension (the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, introduced here) was assumed to be the same as the critical energy release rate, G_c . However, the critical energy release rate, G_c , was developed in linear elastic fracture mechanics (LEFM) [16] and there is very limited plastic work involved. Therefore, the use of G_c as $(dW_p/da)_{cr}$ may not be appropriate for highly ductile materials and has been contested by Ranganathan et al. [42]. In this work, $(dW_p/da)_{cr}$ is assumed to be a different material property and is determined using the method proposed in Nittur et al. [19] by matching an experiment data point with a simulation point.

The second difference is that in Klingbeil [40] the accumulation rate of plastically dissipated energy, dW_p/dN , is calculated from a stationary Model I crack without developing a plastic wake. From Nittur et al. [19], by first developing a plastic wake, the plastically dissipated energy can be calculated more accurately. Therefore, in this work, the method suggested in Nittur et al. [19] is applied to first develop a plastic wake using a node-release scheme and then calculate dW_p/dN .

The first difference from Nittur et al. [19] is that in that work, the crack growth rate is obtained directly from simulation, while in this work the crack growth rate is calculated from simulation using Equation (2.1). With the current method, the overall computation time is reduced as the cycle by cycle simulation in Nittur et al. [19] is not required to determine the crack growth rate.

The second difference is that in Nittur et al. [19] the *total accumulation* of plastically dissipated energy, ΔW^p , in the dissipation domain is used as the criterion that governs crack growth, while here the *accumulation rate* of plastically dissipated energy, dW_p/dN , is used. In the Paris-regime crack growth problem studied here, the crack length is short and the crack growth is small, so dW_p/dN is nearly constant during the crack growth. dW_p/dN can be related to ΔW^p by multiplying by the number of cycles.

The third difference is that even though the term $(dW_p/da)_{cr}$ introduced here has the same physical significance as the W_{cr}^p introduced in Nittur et al. [19], they have slightly different meanings. The W_{cr}^p introduced in Nittur et al. [19] is the critical value of plastically dissipated energy required for *one-element-size increase* in crack length, while the $(dW_p/da)_{cr}$ introduced here is the critical value of plastically dissipated energy required per *incremental increase* in crack length. The difference comes from

the fact that in Nittur et al. [19] a node-release scheme is used to simulate crack propagation (the minimum crack growth is the element size ahead of the crack tip) and to determine the crack growth rate, while here the crack growth rate is calculated from a stationary crack using Equation (2.1). The W_{cr}^p is related to the $(dW_p/da)_{cr}$ by linearly scaling the $(dW_p/da)_{cr}$ with respect to the mesh size at the crack tip.

2.3 Finite Element Model

2.3.1 Model Definition

A standard compact tension (CT) specimen according to ASTM E647 [103] is created using the finite element software package ABAQUS [102] with width W equal 100 mm as shown in Figure 2-2. The model is analyzed with ‘CPE4R’ elements from ABAQUS [102], which are standard 4 node isoparametric, plane strain elements with reduced integration. A structurally refined mesh is defined at the crack tip as shown in Figure 2-2(b). Mesh convergence studies are conducted for each loading and each material to determine the proper element size in the structurally refined mesh area at the crack tip, as will be discussed in Section 2.3.3. The specimen is loaded with a uniform pressure across at the mid-plane of the pin resulting in a cyclic stress load ratio R equal to 0.1.

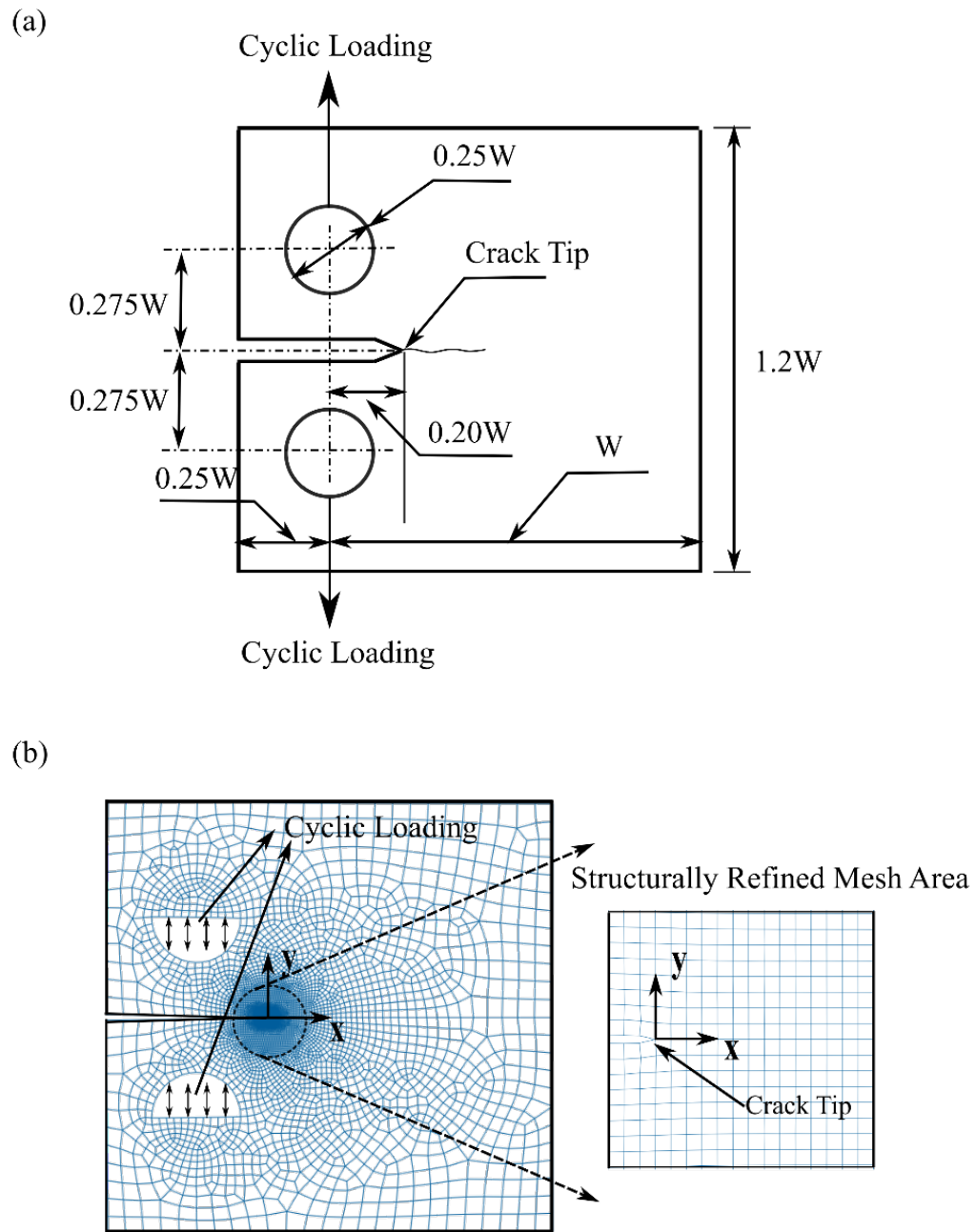


Figure 2-2 (a) ASTM standard for the size of compact tension (CT) specimen [103];
 (b) Two-dimensional finite element model of a compact specimen.

2.3.2 Material Properties

According to Herzberg and Manson [101], there is little influence of loading frequency on the Paris-regime crack growth for PC and Nylon 66. Therefore, the material properties of PC and Nylon 66 are assumed to be elastic-plastic, with incremental, small strain elastoplasticity and a von Mises yield criterion. When the hardening modulus is within 10% of the elastic modulus (typical for highly ductile materials), the strain hardening has very little effect on the plastically dissipated energy under plane strain conditions [40]. Therefore, a linear-elastic, perfect-plastic material behavior is assumed for PC and Nylon 66 in the finite element simulations. The material properties of the specific PC and Nylon 66 used were not provided in Herzberg and Manson [101], so the relevant material properties are taken from web-based material data sheets (provided by Professional Plastics) [104] and are listed in Table 2-1.

Table 2-1 Material properties of PC and Nylon66 [104]

	Elastic Modulus (GPa)	Poisson's Ratio	Yield Strength (MPa)
PC	2.3	0.37	55
Nylon66	3.3	0.41	82

In contrast to the frequency-independent fatigue seen in PC and Nylon, PS, PVC and PMMA have a significant increase in fatigue life (decrease in fatigue crack growth) with increasing load frequency [101]. To capture the rate-dependent behavior, a two-layer viscoelastic-plastic constitutive model provided in ABAQUS [102] with extension by Khattri et al.[105] is applied to model PS, PVC and PMMA. The elastic modulus for PS and PVC exhibits only a minor dependency on the strain rate [101]

and is therefore assumed to be independent of the strain rate. Again, there were no material properties listed for the PS, PVC and PMMA used in Herzberg and Manson [101]. Consequently, material properties of PS, PVC and PMMA are obtained from other sources. The elastic modulus and Poisson's ratio of PS are taken from material property sheets [104,106] and those of PVC are taken from Reference [107], as listed in Table 2-2. The yield stresses for PS [108] and PVC [109] depend significantly on the strain rate, as summarized in Table 2-2. The two-layer viscoelastic-plastic model is fitted for PS and PVC at different strain rates as shown in Figure 2-3. Chen et al. [110] conducted tension tests at different strain rates for PMMA and the two-layer viscoelastic-plastic model is fitted for PMMA at different strain rates as shown in Figure 2-4.

Table 2-2 Material properties of PS and PVC [104,106-109] (room temperature 25 °C (296 K) used for PVC [109])

	Elastic Modulus (GPa)	Poisson's Ratio	Yield Strength (MPa) at selected strain rates			
			0.01	0.1	1	10
PS	3.0	0.35	78	86	94	102
PVC	3.4	0.35	60	65	70	74

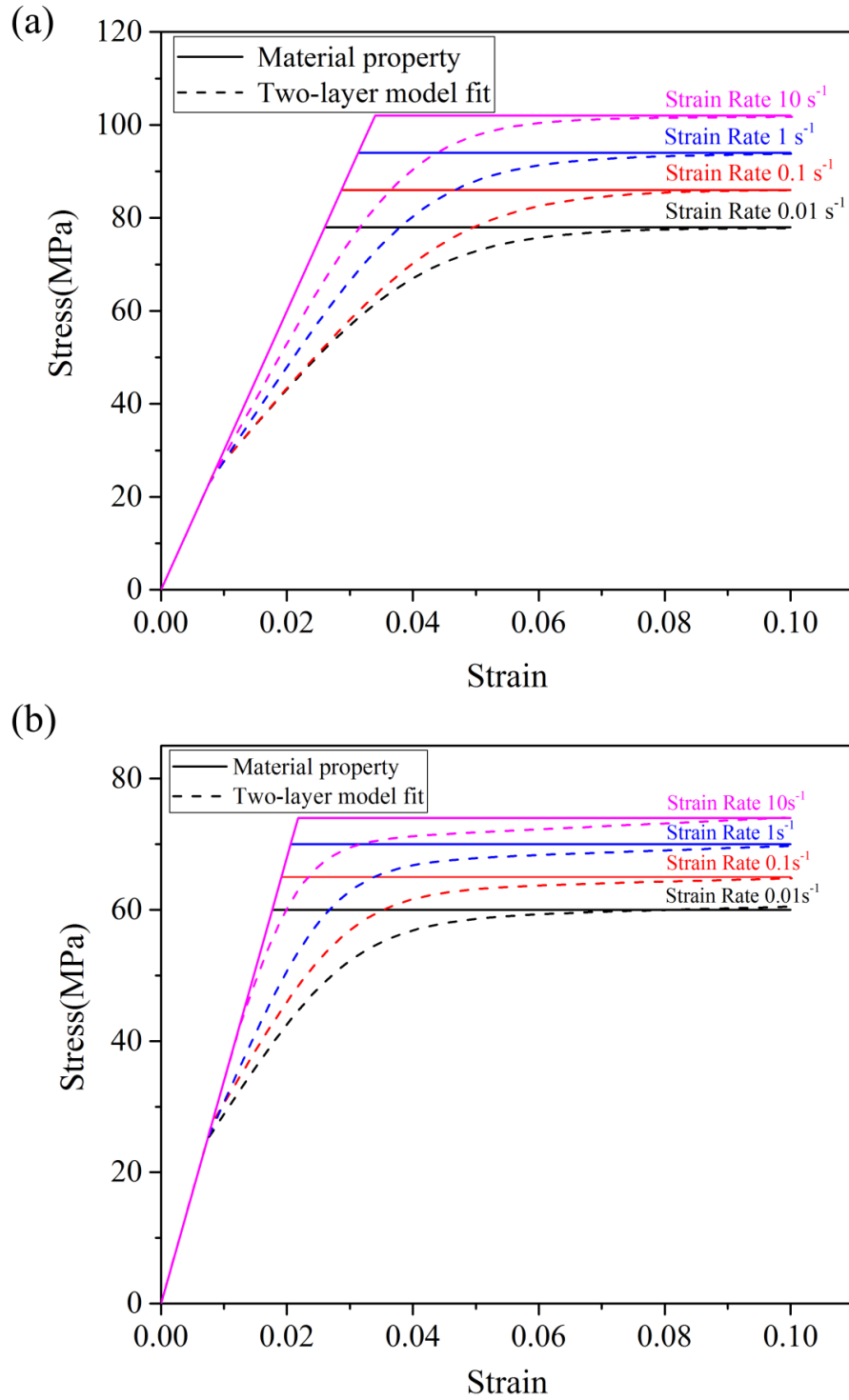


Figure 2-3 (a) Two-layer viscoelastic-plastic model fit of PS and (b) Two-layer viscoelastic-plastic model fit of PVC.

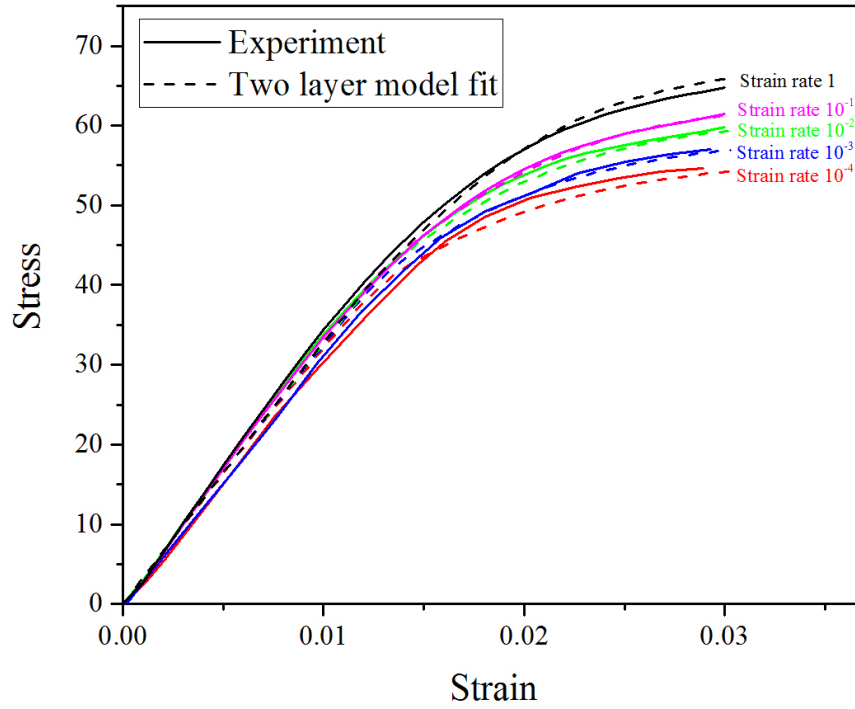


Figure 2-4 Two-layer viscoelastic-plastic model fit of PMMA; Experiment data from Chen et al. [110].

2.3.3 Mesh Convergence

The accumulation of plastically dissipated energy for PC at $\Delta K = 1 \text{ MPa} \sqrt{m}$, in a domain of fixed area ($60 \mu\text{m} \times 60 \mu\text{m}$) is tracked across six different square element sizes ($4 \mu\text{m}$, $3 \mu\text{m}$, $2 \mu\text{m}$, $1 \mu\text{m}$, $0.75 \mu\text{m}$ and $0.5 \mu\text{m}$) in the structurally refined mesh area at the crack tip. Results are plotted in Figure 2-5. The accumulation rate of plastically dissipated energy, dW_p/dN , is calculated as the slope of plastically-dissipated-energy-versus-cycle curve plotted in Figure 2-5.

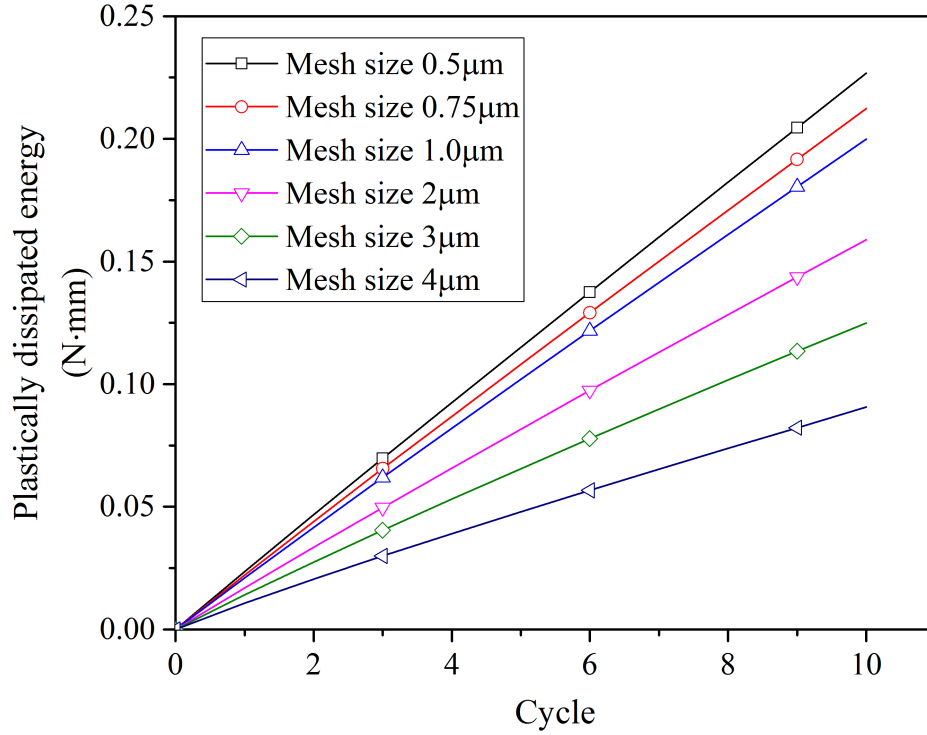


Figure 2-5 Accumulation of plastically dissipated energy in PC at $\Delta K = 1 \text{ MPa} \sqrt{\text{m}}$ as a function of cycles among six different mesh sizes in the structurally refined mesh area at crack tip.

From Figure 2-5, the accumulation rate of plastically dissipated energy, dW_p/dN , for the same-sized dissipation domain for element size of $0.75 \mu\text{m}$ is $2.12\text{E-}2 \text{ N}\cdot\text{mm/cycle}$ and that for element size of $0.5 \mu\text{m}$ is $2.26\text{E-}2 \text{ N}\cdot\text{mm/cycle}$, differing by about 6% and indicating fairly good convergence at this level of refinement. Therefore, the element size in the structurally refined mesh area at the crack tip is chosen to be $0.5 \mu\text{m}$.

Similar mesh convergence studies are conducted for PC at other ΔK values, Nylon 66, PS, PVC and PMMA to determine the proper element size in the structurally refined mesh area at the crack tip.

2.3.4 Node Release Scheme

In this work, a plastic wake is manually developed before tracking dW_p/dN as is suggested in Nittur et al. [19]. To manually develop the plastic wake, node release is applied. Currently, there is no clear consensus on the best timing for node release in simulating crack propagation [111]. Three node release schemes, i.e., at maximum load, at minimum load and immediately after maximum load, were examined in McClung and Sehitoglu [112], and no significant differences were observed among the different schemes. Therefore, following [19,43,44,113,114], in this work, crack propagation is simulated by releasing the ‘Tie Constraint’ in ABAQUS [102] of the nodes at crack tip at minimum load, i.e., at the end of a loading cycle. The hard frictionless contact formulation in ABAQUS [102] is employed to simulate the contact of the crack faces.

2.3.5 Simulation Steps

The simulation steps in the current work are:

1. Select a stress intensity factor range, ΔK ;
2. Develop a fully developed plastic wake by manually propagating the initial crack using node release after every five loading cycles, until the crack has propagated through the initial reverse plastic zone;
3. Record the accumulation rate of plastically dissipated energy $(dW_p/dN)_{sim}$ following the development of the plastic wake;
4. With the experimentally obtained $(da/dN)_{exp}$ corresponding to the same selected ΔK and the corresponding $(dW_p/dN)_{sim}$ calculated in Step 3,

- determine the critical value of plastically dissipated energy required per incremental increase in crack length $(dW_p/da)_{cr}$ using Equation (2.2);
5. Repeat 1-3 for other ΔK values to establish the corresponding accumulation rate of plastically dissipated energy dW_p/dN ;
 6. Use $(dW_p/da)_{cr}$ established in Step 4 to determine the crack growth rate for each ΔK , using Equation (2.1);
 7. Apply a least square power law fit to the calculated crack growth data to construct the Paris-regime crack growth curve and to obtain the Paris coefficients.

2.4 Results and Discussion

2.4.1 Crack Growth Rate for Strain Rate Independent Fatigue

2.4.1.1 Crack Growth Rate for PC

Two polymers that exhibit strain rate independent fatigue crack growth, PC and Nylon 66, are investigated first. Simulation and experimental results for the Paris-regime crack growth rate for PC at four different ΔK levels are presented in Figure 2-6. The experimental data is taken from Hertzberg and Manson [101]. The crack growth rate increases significantly with increasing ΔK levels, e.g., the crack growth for $\Delta K = 6 \text{ MPa } \sqrt{m}$ is three orders larger than that of $\Delta K = 1 \text{ MPa } \sqrt{m}$. If the data is plotted in linear scale (Figure 2-6(a)), the resolution of the plot diminishes since the large difference in magnitude of the crack growth rate at the range of ΔK considered. For example, in Figure 2-6(a), the data points between $\Delta K = 1 \text{ MPa } \sqrt{m}$ and $\Delta K = 2 \text{ MPa } \sqrt{m}$ are difficult to differentiate because of the large crack growth rate at $\Delta K = 6 \text{ MPa } \sqrt{m}$. Plotting the data in log-log scale, as in Figure 2-6(b), avoids the issue and makes the data easier to interpret and to uncover the underlying relationship. This is what was observed by Paris and Erdogan [15] resulting in what is now called “Paris

Law”. It follows that the Paris regime crack growth curves are generally plotted in log-log scale in experimental studies and are also plotted this way here. The critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is determined by matching the experimental data point $(\Delta K, da/dN)$ with the simulation point at $\Delta K = 2 \text{ MPa } \sqrt{m}$. The choice of experimental data point $(\Delta K, da/dN)$ used to determine $(dW_p/da)_{cr}$ has a small effect on the results, as will be discussed later. The numerically calculated crack growth rates for the other ΔK values, as is shown in Figure 2-6(b), are well within the scatter band of the experiment data points in the range where the log-log plot is nearly linear, i.e., where Paris’ Law applies.

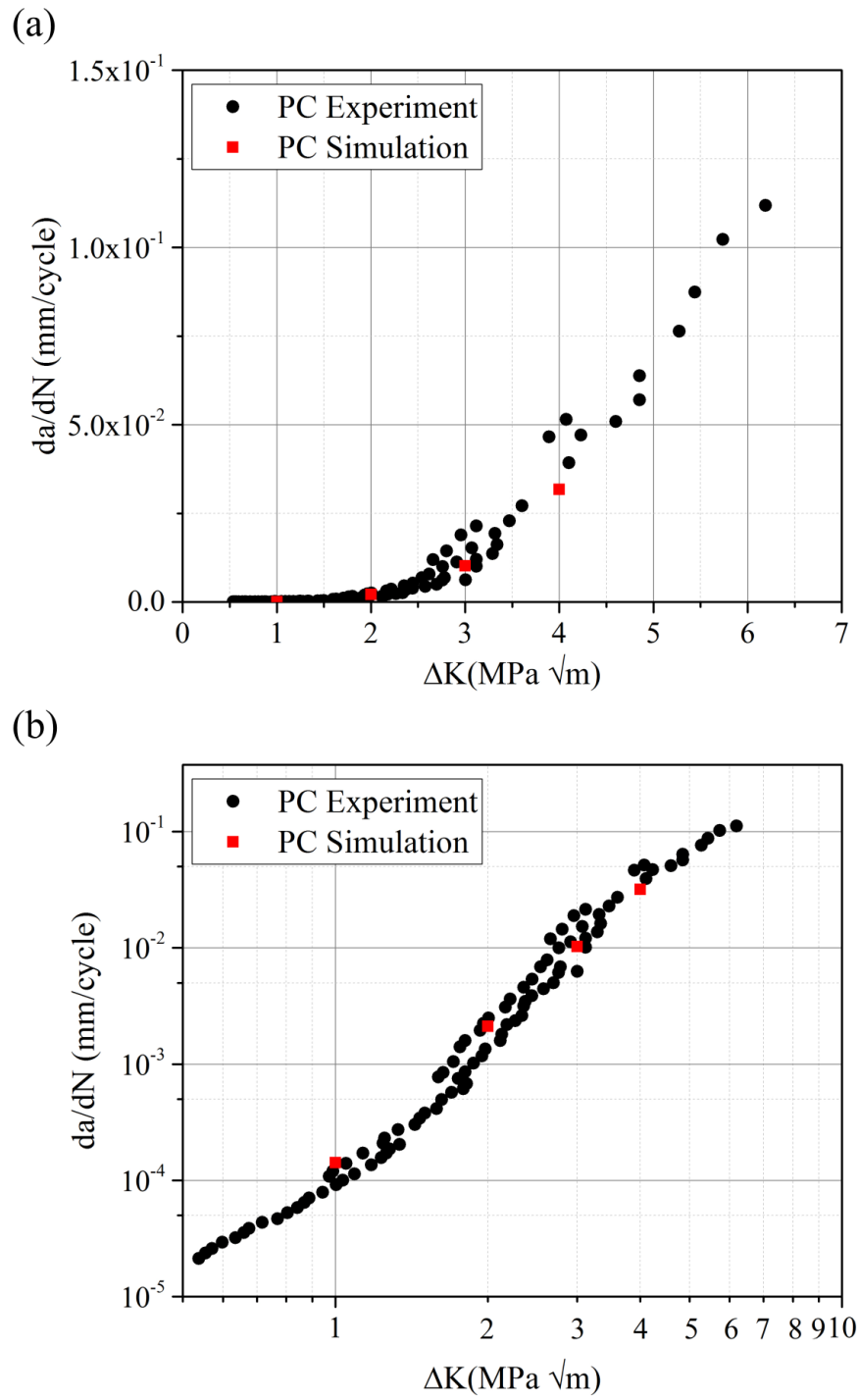


Figure 2-6 Paris-regime crack growth rates of PC at selected ΔK in (a) linear scale and (b) log-log scale. Experiment data points of PC from [101].

A power law fit of the crack growth rate da/dN from the simulation versus the stress intensity factor range ΔK , is used to construct a numerically-generated Paris-regime crack growth curve. Both the numerically-generated Paris-regime crack growth curve and the experimentally-generated one reported in [101] are shown in Figure 2-7. From the plots, the computed Paris-regime crack growth curve matches well with the experimental results reported in [101].

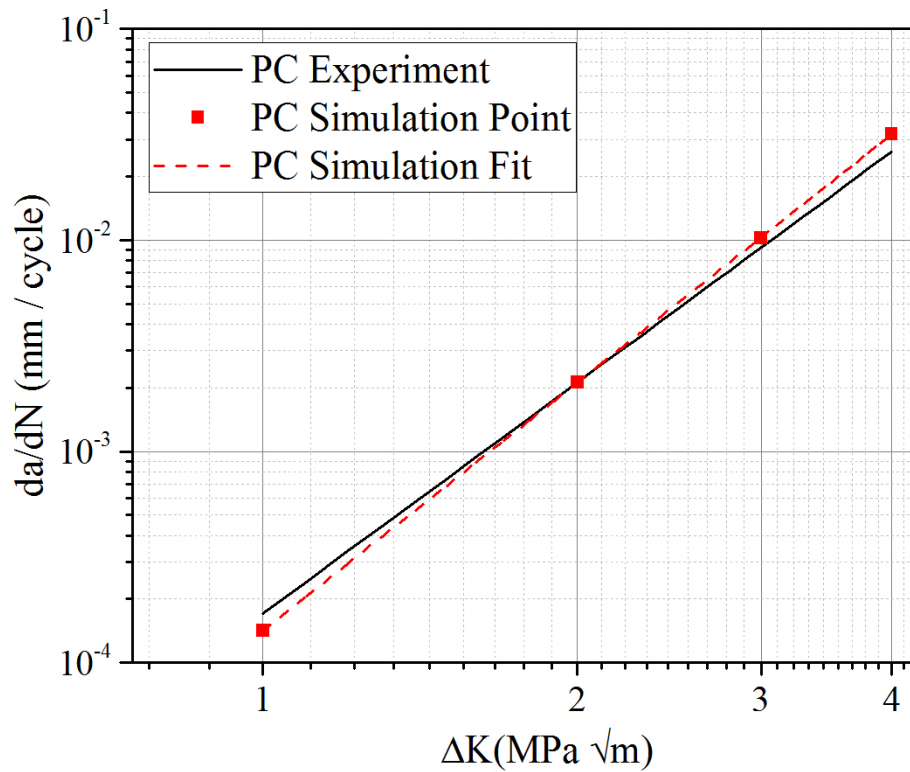


Figure 2-7 Paris-regime crack growth curve reported in [101] and power law fit of the simulation results of PC.

2.4.1.2 Comparison with Crack Growth Rate of PC using the Approach Proposed in Nittur et al. [19]

In order to test the difference between the current method and the one developed in Nittur et al. [19], a comparison of results for PC using both methods is conducted. Recall that the method in Nittur et al. [19] is based on the total accumulation of plastically dissipated energy and a node-release scheme to simulate crack growth. Therefore, if the crack growth rate is large and if a too highly refined mesh is used at the crack tip, there will be several nodes released after each loading cycle, which could lead to numerical instability. On the other hand, if the mesh is too coarse, the model may not be able to accurately calculate the total accumulation of the plastically dissipated energy.

From the experiment results reported in [101], the crack growth rates at four different ΔK values are presented in Table 2-3. For ΔK larger than 2 MPa $\sqrt{\text{m}}$, the crack growth rate is quite large. Therefore, crack growth rate is investigated using the method proposed in Nittur et al. [19] for the ΔK ranging from 1 MPa $\sqrt{\text{m}}$ to 2 MPa $\sqrt{\text{m}}$.

Table 2-3 Crack growth rate of PC at selected ΔK values [101]

ΔK (MPa $\sqrt{\text{m}}$)	da/dN ($\mu\text{m}/\text{cycle}$)
1	0.17
2	2.12
3	9.22
4	26.21

As is stated in Section 2.4.1.1, the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is determined at ΔK equals 2 MPa $\sqrt{\text{m}}$ by matching the experimental data point $(\Delta K, da/dN)$ with the simulation point $(\Delta K, dW_p/dN)$. The $(dW_p/da)_{cr}$ determined this way for PC is 0.164

N·mm/ μm . The same $(dW_p/da)_{cr}$ value is used with the other ΔK values in this section and scaled linearly according to the element size at the crack tip to obtain the critical value of plastically dissipated energy required per one-element-size increase in crack length, W_{cr}^p , used in Nittur's method, as is explained in Section 2.2.3. The load cases with the corresponding element size at the crack tip Δa , W_{cr}^p and the simulated results da/dN are summarized in Table 2-4. The result is compared with the current approach in Figure 2-8 and summarized in Table 2-5.

Table 2-4 Summary of crack growth model parameters and result for PC using the approach proposed in Nittur et al. [19]

ΔK (MPa $\sqrt{\text{m}}$)	Δa (μm)	dW_p/da (N·mm/ μm)	W_{cr}^p (N·mm)	da/dN ($\mu\text{m}/\text{cycle}$)
1	1	0.164	0.164	0.125
1.25	1.5	0.164	0.246	0.3
1.5	2	0.164	0.328	0.667
1.75	3	0.164	0.492	1
2	4	0.164	0.656	2

Table 2-5 Paris coefficient for PC from experiment [101], simulation using Nittur et al. [19] and simulation in current work

	Experiment [101]	Simulation Current	Simulation Nittur et al. [19]
Paris Coefficient C	1.71E-4	1.42E-4	1.26E-4
Paris Coefficient m	3.63	3.90	3.92

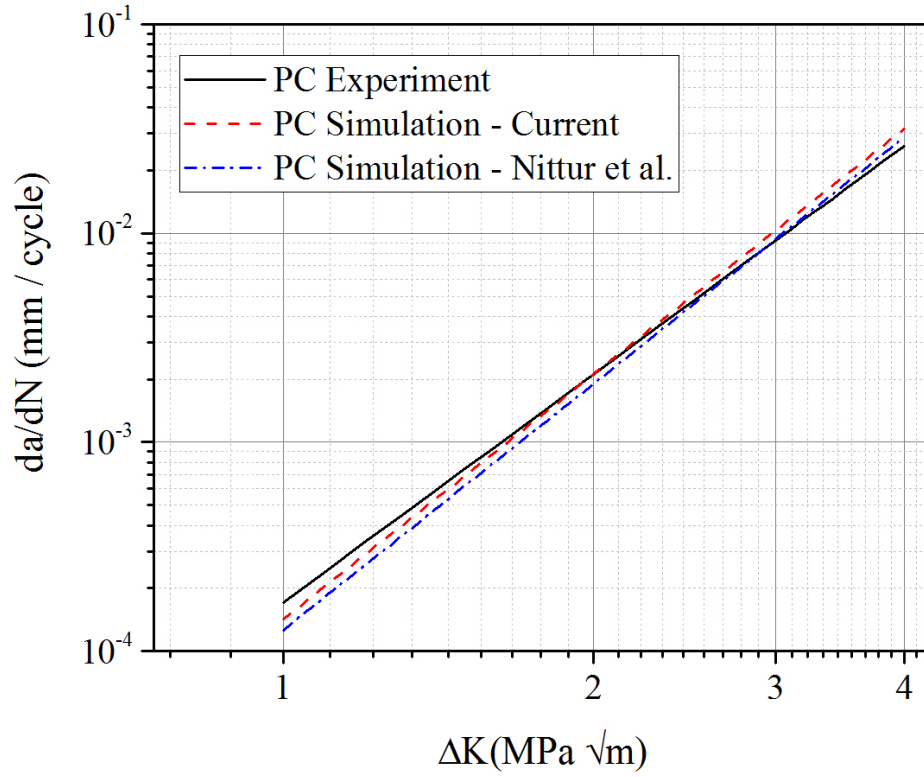


Figure 2-8 Comparison of Paris-regime crack growth curves for PC among experiment [101], simulation using the approach proposed in Nittur et al. [19] and simulation in the current work.

The results using the approach proposed in Nittur et al. [19] and those from the current work are close to each other, since they are based on the same assumption that relates fatigue crack growth with the plastically dissipated energy at the crack tip. The number of cycles required to reach W_{cr}^p will be rounded up to the nearest integer using the approach proposed in Nittur et al. [19], consequently the crack growth rate from the current work is slightly higher than that using the approach proposed in Nittur et

al. [19]. The plastically dissipated energy criterion gives consistent results between the two simulations, despite the use of different numerical implementations.

2.4.1.3 Influence of Data Point Used to Determine $(dW_p/da)_{cr}$

Given that the critical value of plastically dissipated energy per incremental increase in crack length, $(dW_p/da)_{cr}$, is assumed to be a material property, it must therefore be determined from experiments. In the current study, the value of this material property is determined by selecting a ΔK value and matching the experimentally determined data point ($(\Delta K, da/dN)$ from the literature) with a numerically determined data point ($(\Delta K, dW_p/dN)$ from the simulations) using Equation (2.2). Figure 2-9 shows the Paris-regime crack growth curves generated numerically for PC, using experimental values of da/dN at four different ΔK values to determine $(dW_p/da)_{cr}$. The value of ΔK selected to determine $(dW_p/da)_{cr}$ has only a small effect on the Paris-regime crack growth curves. These results show that the choice of different ΔK values affects the value of parameter C in Paris' Law (Equation (1.2)), but the value of parameter m remains the same (i.e., the lines are parallel on a log-log plot). However, this minor dependency in C is well within the scatter of the experimental data.

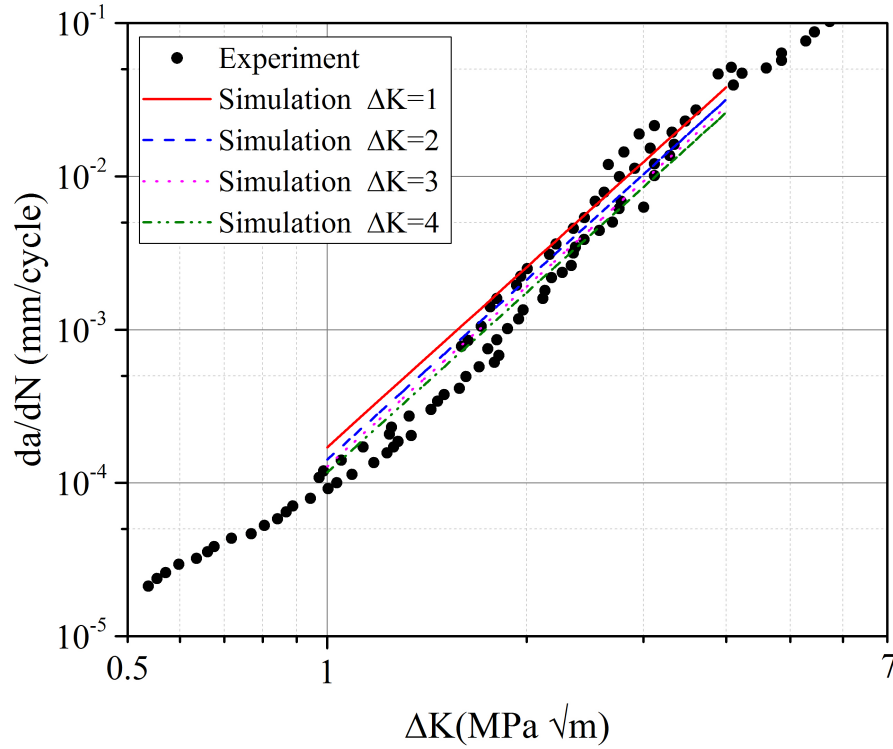


Figure 2-9 Power law fit of the numerical predicted Paris-regime crack growth curves. Experiment data points from [101].

2.4.1.4 Crack Growth Rate for Nylon 66

Using the method proposed in the current work, a Paris-regime crack growth curve is also constructed for Nylon 66. The critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, for Nylon 66 is determined at $\Delta K = 2 \text{ MPa} \sqrt{m}$. The Paris-regime crack growth curve constructed from the simulation and that reported from experimental results in [101] are both shown in Figure 2-10 and again, there is a good agreement.

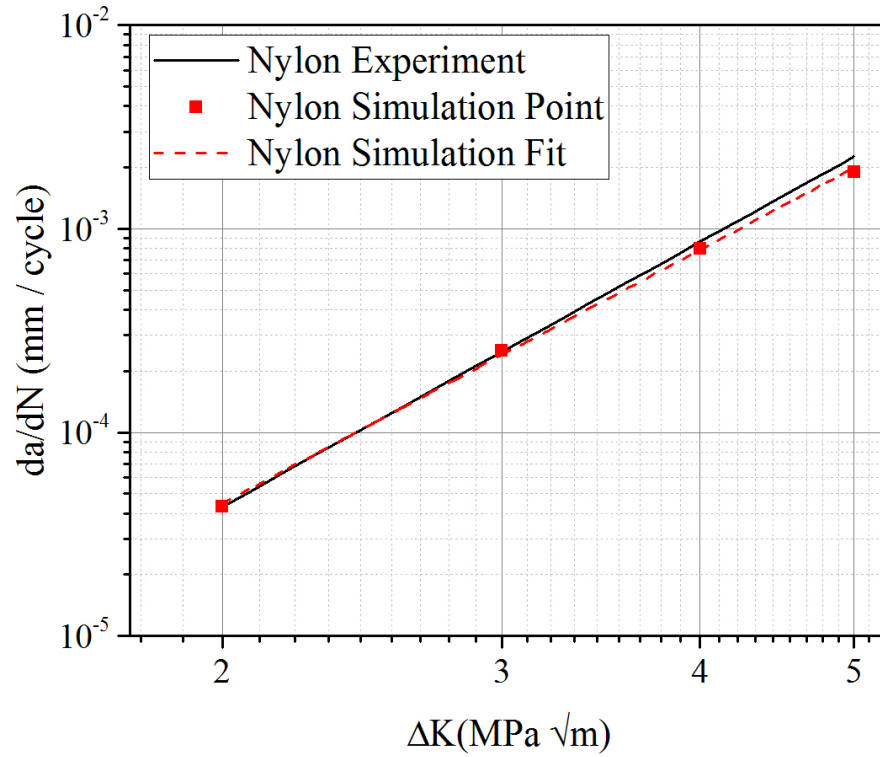


Figure 2-10 Paris-regime crack growth curve reported in [101] and power law fit of the simulation results of Nylon 66.

2.4.2 Crack Growth Rate for Strain Rate Dependent Fatigue

2.4.2.1 Crack Growth Rate for PS

Next, polymers with fatigue properties that are dependent on the load frequency [101] are investigated, starting with PS[‡]. As described previously, the two-layer viscoelastic plastic constitutive model [102] with extension by Khattra et

[‡] No information is provided in Reference [101] regarding the temperature change or thermal effects induced by the cyclic loading or by the change in loading frequency. Therefore, thermal effects are not considered in this work for PS, PVC and PMMA.

al.[105] is used to characterize the response of PS. For PS, the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is determined at $\Delta K = 0.25 \text{ MPa } \sqrt{\text{m}}$ at 1Hz and is assumed to be the same for all other ΔK values and all other frequencies. The Paris-regime crack growth curves for PS at three different frequencies are shown in Figure 2-11. As can be seen from the figure, the predicted response is close to the experimental values. Note that the simulation fits the experimental data well at 10 Hz and 100 Hz even though $(dW_p/da)_{cr}$ was determined from the 1 Hz experimental data.

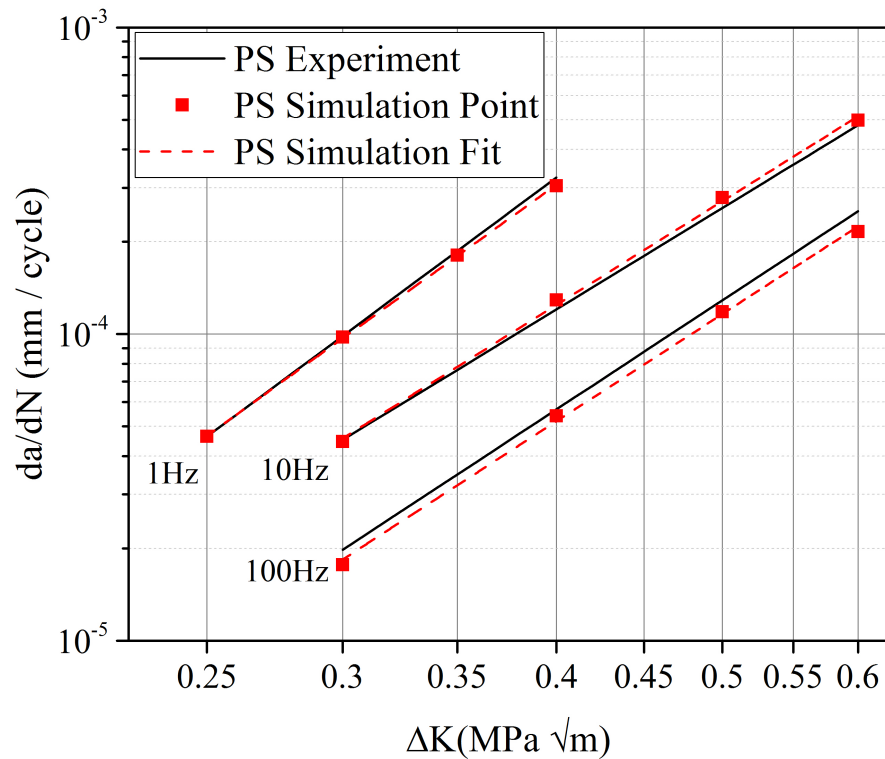


Figure 2-11 Paris-regime crack growth curve reported in [101] and power law fit of the simulation results of PS.

2.4.2.2 Comparison with Crack Growth Rate of PS using the Approach Proposed in Nittur et al. [19]

As is stated in Section 2.4.2.1, the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is assumed to be the same for all ΔK values and all frequencies (The value used for PS is $3.38\text{E-}3 \text{ N}\cdot\text{mm}/\mu\text{m}$ as determined at $\Delta K = 0.25 \text{ MPa}\sqrt{\text{m}}$). This value is scaled linearly according to the mesh size at the crack tip to obtain the critical value of plastically dissipated energy W_{cr}^p used in Nittur's method, as is explained in Section 2.2.2. Each load case with its corresponding mesh size at the crack tip, W_{cr}^p and the simulated results da/dN are summarized in Table 2-6. The results are compared with the current approach in Figure 2-12 and summarized in Table 2-7. Again, a close match is found between the simulation results using the approach in Nittur et al. [19] and simulation results using the current implementation.

Table 2-6 Summary of crack growth model parameters and result for PS using the approach proposed in Nittur et al. [19]

Frequency	ΔK (MPa $\sqrt{\text{m}}$)	Δa (μm)	dW_p/da (N $\cdot$ mm/ μm)	W_{cr}^p (N $\cdot$ mm)	da/dN ($\mu\text{m}/\text{cycle}$)
1Hz	0.3	0.45	3.38E-3	1.52E-3	0.09
	0.33	0.55	3.38E-3	1.86E-3	0.138
	0.36	1	3.38E-3	3.38E-3	0.2
	0.4	1.2	3.38E-3	4.06E-3	0.3
10Hz	0.4	0.7	3.38E-3	2.37E-3	0.117
	0.5	1	3.38E-3	3.38E-3	0.25
	0.55	1	3.38E-3	3.38E-3	0.333
	0.6	1.5	3.38E-3	5.07E-3	0.50
100Hz	0.45	0.55	3.38E-3	1.86E-3	0.079
	0.5	0.7	3.38E-3	2.37E-3	0.117
	0.55	1	3.38E-3	3.38E-3	0.167
	0.6	1.5	3.38E-3	5.07E-3	0.214

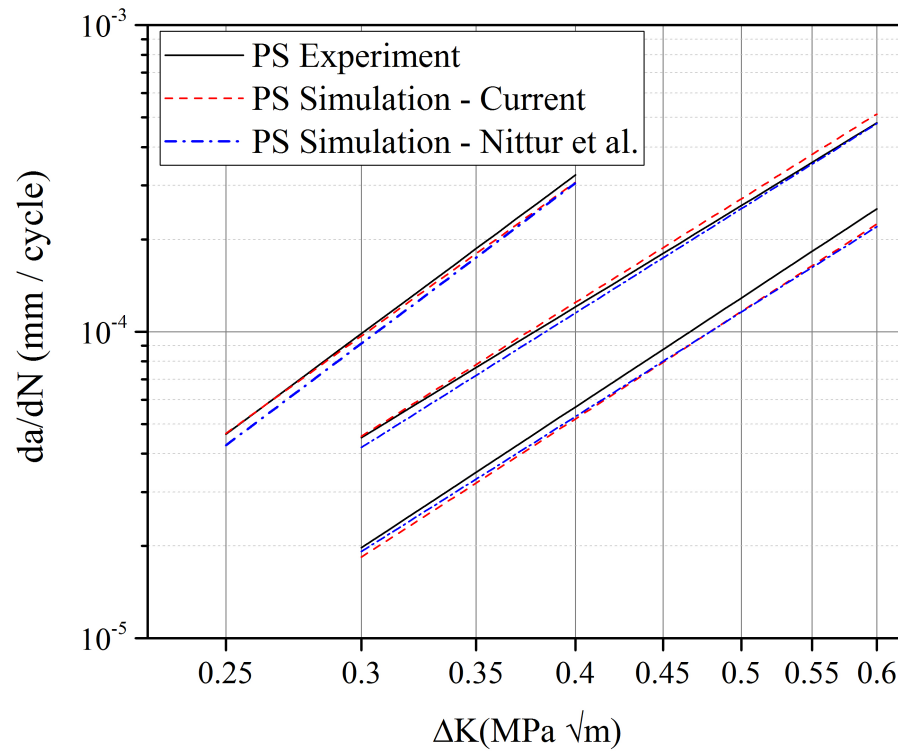


Figure 2-12 Comparison of Paris-regime crack growth curves for PC among experiment [101], simulation using the approach proposed in Nittur et al. [19] and simulation in the current work.

Table 2-7 Paris coefficient from PS from experiment [101], simulation using Nittur et al. [19] and simulation in current work

		Experiment [101]	Simulation Current	Simulation Nittur et al. [19]
1Hz	Paris Coefficient C	1.44E-2	1.21E-2	1.42E-2
	Paris Coefficient m	4.14	4.01	4.19
10Hz	Paris Coefficient C	2.74E-3	3.05E-3	2.87E-3
	Paris Coefficient m	3.41	3.49	3.51
100Hz	Paris Coefficient C	1.64E-3	1.42E-3	1.33E-3
	Paris Coefficient m	3.67	3.61	3.52

2.4.2.3 Crack Growth Rate for PVC

As described previously, the two-layer viscoelastic plastic constitutive model [102] with extension by Khattri et al.[105] is applied to characterize load response of PVC. The critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is determined at $\Delta K = 0.6 \text{ MPa} \sqrt{m}$ at 1Hz and is assumed to be the same for all other ΔK values and all other frequencies. The Paris-regime crack growth curves for PVC at three different frequencies are shown in Figure 2-13. As can be seen from the Figure 2-13, the predicted response is close to the experimental values.

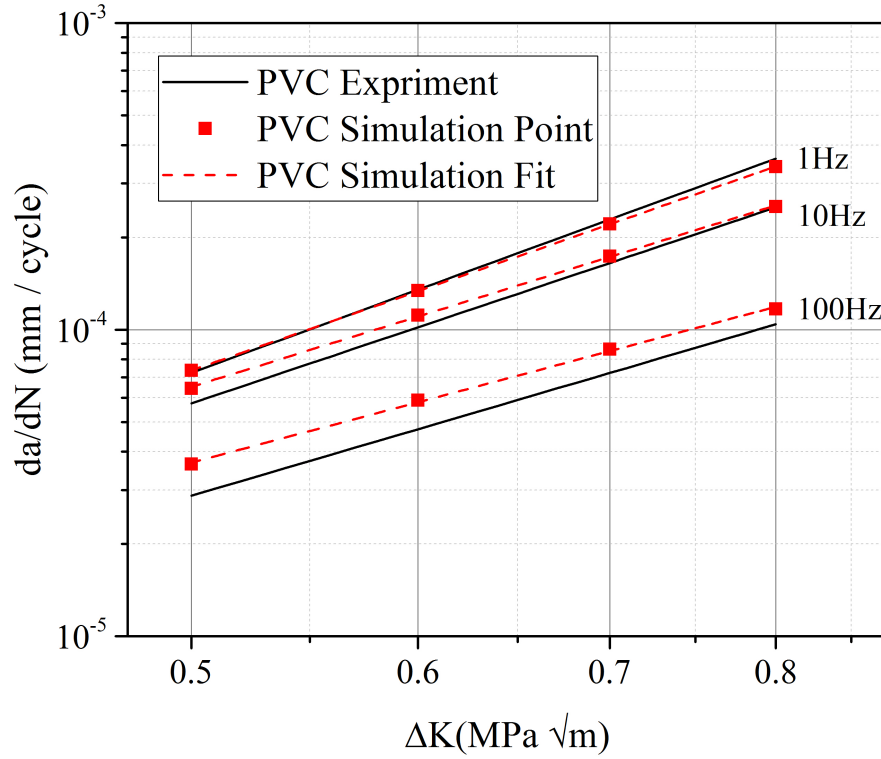


Figure 2-13 Paris-regime crack growth curve reported in [101] and power law fit of the simulation results of PVC.

2.4.2.4 Crack Growth Rate for PMMA

As a third example, the two-layer viscoelastic plastic constitutive model [102] with extension by Khattri et al.[105] is implemented to characterize load response of PMMA. The critical value of plastically dissipated energy required per incremental increase in crack length $(dW_p/da)_{cr}$ is determined at $\Delta K = 0.6 \text{ MPa } \sqrt{m}$ at 0.5 Hz and is assumed to be the same for all other ΔK values and all other frequencies. The Paris-regime crack growth curves for PMMA at four different frequencies are shown in Figure 2-14.

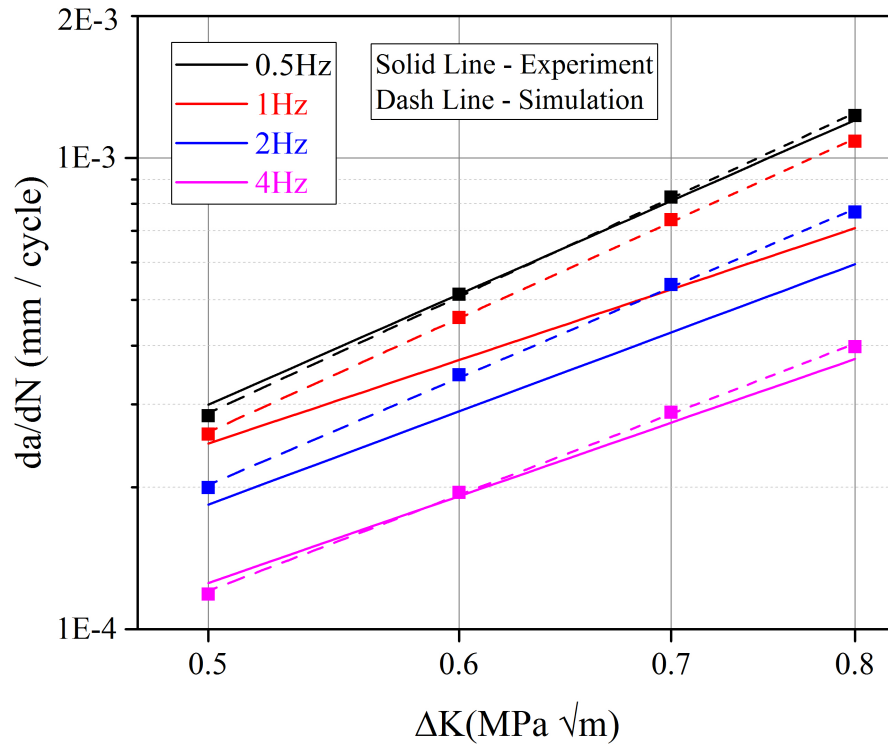


Figure 2-14 Paris-regime crack growth curve reported in [101] and power law fit of the simulation results of PMMA.

As can be seen from Figure 2-14, the predicted response is close to the experimental values for load frequencies 0.5 Hz and 4 Hz, but is not as close for the experimental results of 1 Hz and 2 Hz. The fact that the exact material properties of the PMMA used in the experiment are not listed in [101] and the relevant material properties used in simulations are taken from other open resources, may lead to the mismatch. Also, in the experimental paper (Chen et al. [110]) from which the relevant material properties of PMMA are obtained, the difference in strain rate for each experimental data is 10, so the experimental material property data is not able to fully

resolve the strain rate difference induced by loading frequencies 0.5 Hz and 1Hz (factor of 2) and that induced by loading frequencies 0.5 Hz and 2Hz (factor of 4).

2.4.3 Summary

The predicted values of the Paris coefficients, C and m , are summarized in Table 2-8 for the various materials investigated in this study. From the table, it is evident that the simulation results agree well with the reported experimental results for all materials and at all frequencies. The coefficient C shows a difference of up to about 20% (except for the cases of PMMA at 1Hz and 2Hz discussed Section 2.4.2.4), but the simulation values and experimental values are all of the same order of magnitude. The more important exponent coefficient, m , is within 10% (except for the cases of PMMA at 1Hz and 2Hz) for the materials investigated.

Table 2-8 Paris coefficients from experiment [20] and simulation

(a)

	Paris Coefficient C		
	Experiment	Simulation	Difference
PC	1.71E-4	1.42E-4	17.0%
Nylon 66	2.16E-6	2.54E-6	17.6%
PS 1Hz	1.44E-2	1.21E-2	16.0%
PS 10Hz	2.74E-3	3.05E-3	11.3%
PS 100Hz	1.64E-3	1.42E-3	13.4%
PVC 1Hz	7.75E-4	7.06E-4	8.9%
PVC 10Hz	5.04E-4	4.86E-4	3.6%
PVC 100Hz	1.92E-4	2.07E-4	7.8%
PMMA 0.5Hz	2.33E-3	2.50E-3	7.3%
PMMA 1Hz	1.17E-3	2.17E-3	85.5%
PMMA 2Hz	1.04E-3	1.48E-3	42.3%
PMMA 4Hz	6.30E-4	7.16E-4	13.7%

(b)

	Paris Coefficient m		
	Experiment	Simulation	Difference
PC	3.63	3.90	7.4%
Nylon 66	4.32	4.14	4.2%
PS 1Hz	4.14	4.00	3.1%
PS 10Hz	3.41	3.48	2.3%
PS 100Hz	3.67	3.61	1.6%
PVC 1Hz	3.42	3.26	4.7%
PVC 10Hz	3.13	2.90	7.3%
PVC 100Hz	2.74	2.52	8.0%
PMMA 0.5Hz	2.96	3.12	5.4%
PMMA 1Hz	2.24	3.05	36.2%
PMMA 2Hz	2.50	2.87	14.8%
PMMA 4Hz	2.33	2.57	10.3%

2.5 Synopsis

The original contribution to the literature that this chapter makes is the extension of a numerical scheme to predict fatigue crack growth rate based on the accumulation rate of plastically dissipated energy ahead of a crack tip. The numerical scheme developed here reduces the computation time of the scheme proposed in Nittur et al. [19]. Furthermore, the new scheme extends the use of the plastically dissipated energy criterion from studying fatigue crack growth in metals, as in Klingbeil [40] and Nittur et al. [19], to its use in studying fatigue crack growth in polymers. The proposed numerical scheme is applied to investigate Paris-regime crack growth in two classes of polymers, those exhibiting frequency-*independent* fatigue crack growth and those exhibiting frequency-*dependent* fatigue crack growth. The proposed method can even be used to estimate fatigue crack growth for a wider range of ductile materials based on limited fatigue testing and could therefore potentially reduce the cost and time of introducing new materials in engineering structures.

The crack growth rate, da/dN , is assumed to be the accumulation rate of plastically dissipated energy, dW_p/dN , divided by the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, as described in Equation (2.1). The dW_p/dN at different ΔK levels are obtained by probing the accumulation of plastically dissipated per load cycle in a dissipation domain that fully captures the initial reverse plastic zone using a two-dimensional finite element model of a standard compact tension (CT) specimen under plane strain conditions. The $(dW_p/da)_{cr}$ is assumed to be a material property and is obtained by matching one experimental point (ΔK , da/dN) with a simulation point (ΔK , dW_p/dN), using Equation (2.2). Once $(dW_p/da)_{cr}$ is established, the crack growth rate da/dN can be determined with Equation (2.1) and the Paris-regime curves can then be constructed.

Numerical results are presented for PC and Nylon 66, whose Paris-regime crack growth behavior is independent of testing frequency, and for PS, PVC and PMMA, whose Paris-regime crack growth behavior is dependent on testing frequency. The numerically predicted Paris-regime crack growth curves are in good agreement with experimentally obtained Paris-regime crack growth curves for both the frequency-independent and frequency-dependent polymers studied.

After verifying the capability of the plastically dissipated energy criterion in studying fatigue crack growth in polymers, in the next chapter, the numerical scheme is extended to study the crack growth in polymer electrolyte membranes under relative humidity (RH) cycles.

Chapter 3

NUMERICAL EVALUATION OF CRACK GROWTH IN POLYMER ELECTROLYTE FUEL CELL MEMBRANE BASED ON PLASTICALLY DISSIPATED ENERGY

3.1 Introduction

Understanding the mechanisms of growth of defects in polymer electrolyte membrane (PEM) fuel cells is essential for improving cell longevity. Characterizing the crack growth in PEM fuel cell membranes under relative humidity (RH) cycling is an important step towards establishing strategies essential for developing more durable membrane electrode assemblies (MEAs). Currently, there is very little work on modeling *in-situ* crack growth in polymer electrolyte membranes in the literature.

In the last chapter, the results show that the plastically dissipated energy criterion is able to capture the fatigue crack growth behavior of a variety of polymers, thus showing the possibility of expanding the methodology to simulate other polymers under a wider range of loadings. Therefore, in this chapter, the plastically dissipated energy criterion is extended to investigate *in-situ* fatigue crack growth in the through-thickness direction of polymer electrolyte membranes under humidity cycling. A range of well-established experimental observations are studied including: a) crack propagation in unreinforced perfluorosulfonic acid (PFSA) membranes, b) crack propagation in expanded polytetrafluoroethylene (ePTFE) reinforced PFSA membranes, c) the differences between crack propagation under the channel and land regions in a typical flow channel architecture, d) the effect of fuel cell clamping

pressure on membrane cracking and e) the effect of different RH cycles on the number of cycles to failure under accelerated mechanical testing.

3.2 Numerical Framework

3.2.1 General Concepts

In Paris-regime crack growth, the crack is relatively short and the increase in crack length has little influence on the accumulation rate of plastically dissipated energy, dW_p/dN . However, for through cracks in polymer electrolyte membranes under relative humidity (RH) cycling, the crack growth is large and the crack length after growth is comparable to the thickness of the membrane, so Paris law behavior is not applicable. The methods in Nittur et al. [19] have been applied to study large crack growth in [44]. Therefore, in this chapter a numerical scheme similar to the one in Nittur et al. [19] is implemented to calculate the actual accumulation of plastically dissipated energy in the dissipation domain around the crack tip, ΔW^p , and compare this with a pre-determined critical value of plastically dissipated energy, W_{cr}^p .

In the case of *in-situ* loading of PFSA, plastic energy is dissipated throughout a large portion of the PSFA membrane during any particular load cycle [68-71]. To address this, a systematic investigation on the ratio of plastically dissipated energy near versus away from the crack tip was conducted, which is discussed in Section 3.3.7. It was found that there is significantly greater accumulation of plastically dissipated energy near the crack tip. Therefore, the appropriate size of the dissipation domain in this study was chosen to capture the majority of the plastically dissipated energy increment around the crack tip, yet not to have that increment obscured by the increase in plastically dissipated energy in the rest of the membrane.

3.2.2 Propagation Scheme

In the following section, a finite element (FE) model of a representative volume element of a polymer electrolyte membrane (PEM) fuel cell is described where the exposed surface area within the bipolar plate flow channel is loaded by applying a relative humidity (RH) cycle to simulate accelerated mechanical testing. At the end of each RH loading cycle, the accumulation of plastically dissipated energy in the dissipation domain, ΔW^p , is calculated and compared with the critical value of plastically dissipated energy, W_{cr}^p . As noted earlier, W_{cr}^p is an as-yet undetermined material property and is therefore given an assumed value in this study. If $\Delta W^p < W_{cr}^p$, the crack tip remains in its current location and another loading cycle is applied. If $\Delta W^p \geq W_{cr}^p$, the crack propagates along the pre-defined crack path. In this work the crack is assumed to propagate along a straight line in the through-thickness direction. This crack path is based on experimental observations which suggest that through the thickness is a prevalent crack path in a polymer electrolyte fuel cell membrane under RH cycling (for example see Figure 1-5). In addition, from previous simulations [68-71], it was shown that in-plane stress is the dominant stress in the membrane during humidity cycling. As a result, Mode I crack growth is the dominant crack growth mode for through-thickness cracks. The propagation of the crack is implemented by a node-release scheme and consequently the introduction of a new increment of crack surface. Once the crack propagates, the dissipation domain is moved to correspond to the new crack tip location and the accumulation of plastically dissipated energy is determined in the new dissipation domain. If the accumulation of plastically dissipated energy inside the new domain is still above the critical value of plastically dissipated energy, another node is released and the plastically dissipated energy criterion is again assessed. This is repeated until the accumulation of plastically

dissipated energy in the region is below the critical value of plastically dissipated energy, at which time the crack stops propagating for this load increment and a new loading cycle is simulated. This algorithm is illustrated in the flow chart depicted in Figure 3-1. Following this procedure, the crack length as a function of cycle number, can be obtained from the finite element simulation.

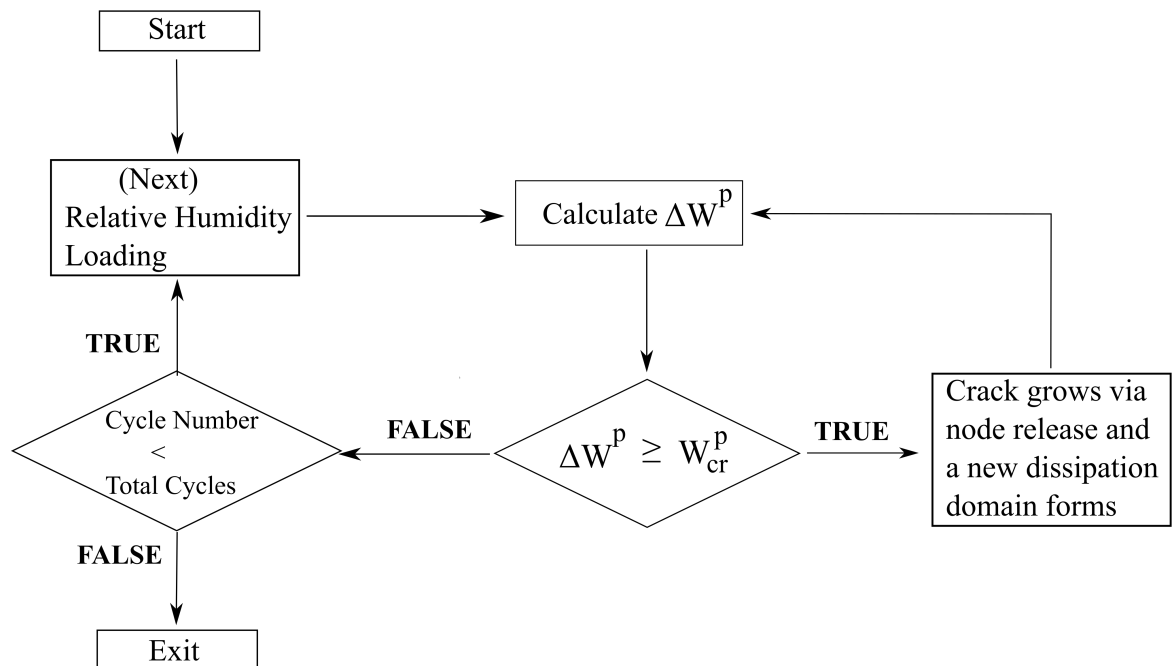


Figure 3-1 Flow chart of the node-release scheme for crack propagation analysis.

3.3 Finite Element Model

3.3.1 Geometry

Two-dimensional plane strain models are created for representative unit volumes of a PEM fuel cell using the commercial finite element package ABAQUS

[102]. The specific geometry of the models used in this study are adapted from previous work [68-70,76] and a sample model is illustrated in Figure 3-2.

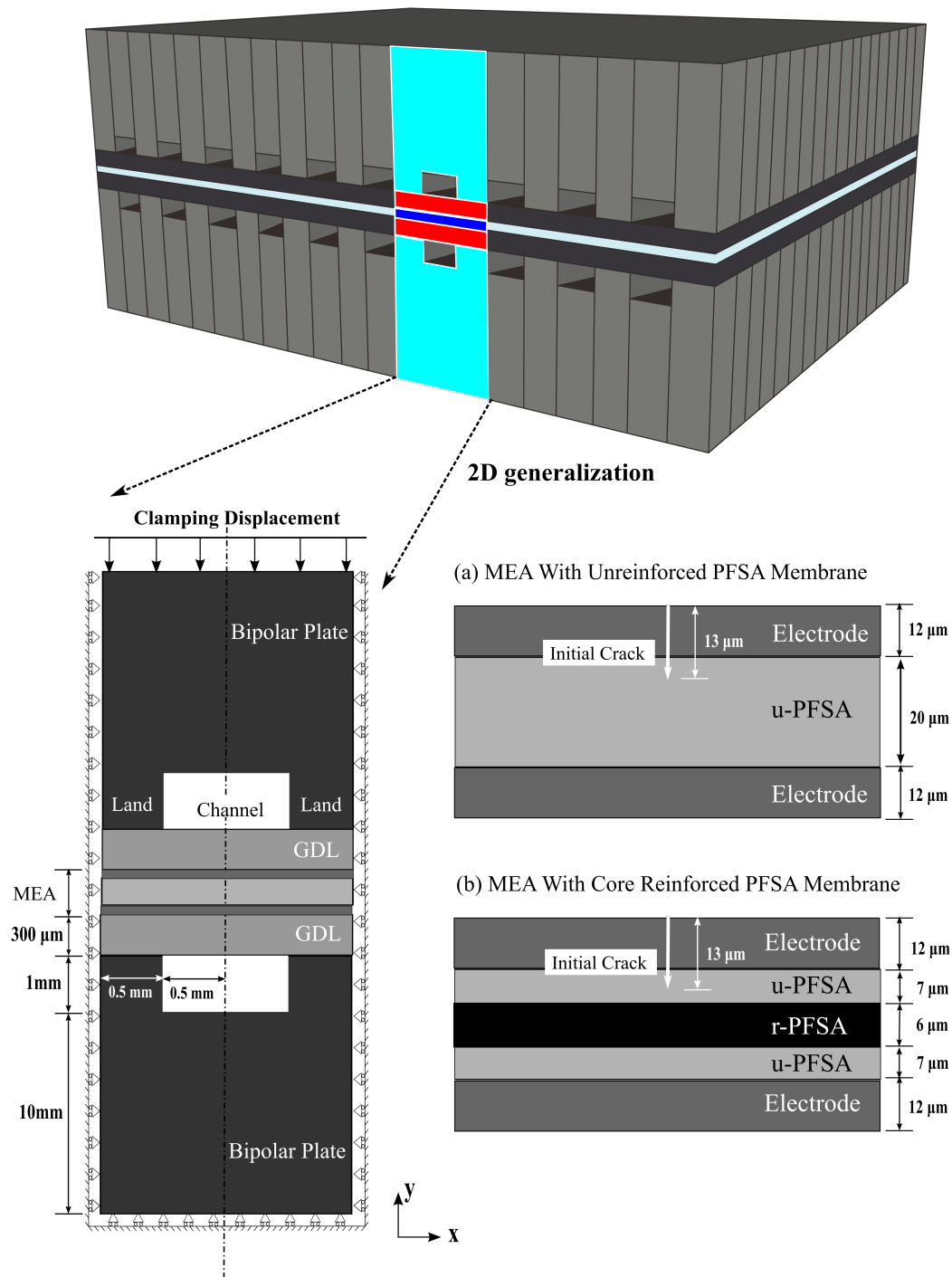


Figure 3-2 Two-dimensional representative model of a fuel cell unit (not to scale) [68-70,76].

Repetitive lands and grooves of bipolar plates form the gas channels in a fuel cell unit volume. For this specific example geometry, the finite element model consists of two half lands and one whole channel. The right edge and the left edge have symmetric boundary conditions applied to represent the repeating of the land-groove geometry. A fixed clamping displacement, to prevent any overall expansion in the thickness direction (y -direction in the FE model), is applied to the top surface in Figure 3-2, corresponding to a fuel cell stack clamped by the tightening of bolts. A symmetry boundary condition is applied to the bottom surface. For the results and discussion in Section 3.4.1, 3.4.2 and 3.4.3, the clamping displacement applied is zero, meaning that the top surface is fixed at no load during ambient conditions. In Section 3.4.4, the influence of different clamping conditions is discussed.

Two types of membrane electrode assembly (MEA) are modeled. MEAs containing only unreinforced PFSA ionomer (u-PFSA) membranes are modeled as a three-layer sandwich structure with electrodes coated onto both sides of unreinforced PFSA [41]. MEAs with core reinforced PFSA membranes are modeled as a five-layer structure with a layer of reinforced PFSA (r-PFSA) in the middle of the membrane region [42]. The electrodes, unreinforced PFSA (u-PFSA) and reinforced PFSA (r-PFSA) are all assumed perfectly bonded [40]. A pre-existing crack of length $13\text{ }\mu\text{m}$ is assumed, which extends through one electrode ($12\text{ }\mu\text{m}$ thick) and $1\text{ }\mu\text{m}$ into the PFSA membrane. The focus of this work is the propagation of the crack and therefore the initiation of the crack is not simulated. The initial crack length is selected to be $13\text{ }\mu\text{m}$ since the aim is to test the viability of the plastically dissipated energy criterion by studying experimental observations qualitatively using simulations, and preliminary

studies showed that different choices of initial crack length don't affect the general trend shown in Section 3.4.

To compare crack growth in different regions of the PEM fuel cell, the finite element model in Figure 3-2 is modified to include one whole land and two half channels as illustrated in Figure 3-3. An initial crack of the same length (13 μm) is assumed in this model under the land region.

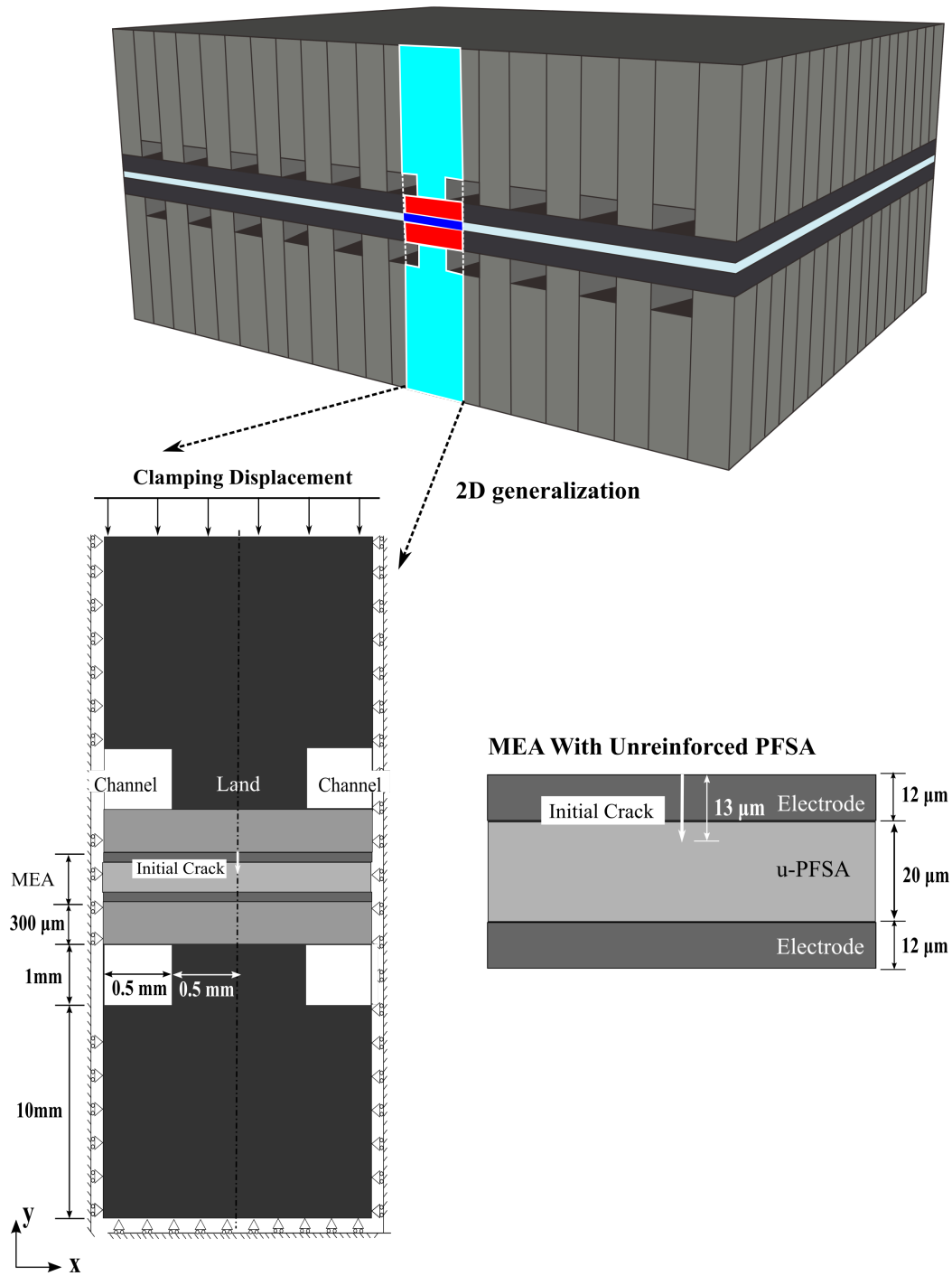


Figure 3-3 Two-dimensional representative model of the fuel cell unit with one whole land and two hand channels containing MEA with unreinforced PFSA membrane (not to scale) [68-70,76].

3.3.2 Assumptions

The following assumptions are made in the finite element models in Figure 3-2 and Figure 3-3:

1. Interfaces between different components, such as the interface between electrodes and membrane, the interface between electrodes and gas diffusion layers (GDLs) and the interface between GDLs and bipolar plates, are assumed to be perfect. The 'Tie Constraint' in ABAQUS [102] is applied to simulate the perfect bonding.
2. A pre-existing crack is assumed. The crack is located at the middle of the channel or land and is 13 μm long (extending from the anode into the membrane). Crack initiation is not considered here and only crack propagation is investigated. Non-penetrating, frictionless contact properties ('Frictionless' and 'Hard Contact' options in ABAQUS [102]) are used to simulate the interaction between crack faces.
3. The crack is assumed to propagate along a pre-defined straight line in the through-thickness direction. This crack path is based on experimental observations which suggest that through the thickness is the prevalent crack path for a fuel cell membrane under relative humidity (RH) cycling (for example see Figure 1-5). In addition, from previous simulations [68-71], it has been shown that in-plane stress is the dominant stress in the membrane during RH cycling. As a result, Mode I crack growth is the dominant crack growth mode for through-thickness.
4. In the case of crack propagation in rPFSA membrane (see Figure 3-2 for the geometry of the rPFSA membrane), the crack does not reach the interface of PFSA membrane and ePTFE reinforcement. It is possible that after it reaches the interface, the crack continues to grow through the thickness or along the interface. This is not considered in this work.
5. The system is driven by changes in temperature and water content, which swell and contract the membrane. No chemical reaction is simulated, so heat generation and water generation are neglected.

3.3.3 Material Properties

The material properties of the components in the finite element model are as follows:

1. The bipolar plates are graphite, modeled as linear elastic with elastic modulus of 10 GPa and Poisson's ratio of 0.25 [41]. Hygrothermal expansion is neglected.
2. The gas diffusion layers (GDLs) are commercially available porous, carbon-fiber GDLs, modeled as linear elastic and transversely isotropic with in-plane elastic modulus of 1500 MPa, out-of-plane elastic modulus of 9 MPa, and Poisson's ratio of zero [76]. Hygrothermal expansion is neglected. The water diffusion coefficient of the GDLs is adopted from [53,115,116].
3. The electrodes are porous carbon-supported PFSA and platinum, modeled as viscoelastic-plastic with material property parameters determined in Lu et al. [117]. Hygrothermal expansion is also neglected. The water diffusion coefficient of the electrodes is assumed to be the same as the unreinforced PFSA (u-PFSA) [54,76].
4. The unreinforced PFSA (u-PFSA) has viscoelastic-plastic material property parameters determined in Khattra et al. [76], and Poisson's ratio of 0.4 [118]. The PFSA membrane is the only component that experiences hygrothermal expansion and the hygrothermal expansion is assumed to be isotropic for simplicity. The water diffusion coefficient of u-PFSA is adopted from [53,119,120].
5. When the model includes core reinforced PFSA membrane, the reinforced PFSA (r-PFSA) is modeled as viscoelastic-plastic with material property parameters determined in Khattra et al.[105]. The water diffusion coefficient of r-PFSA is adopted from [53,54].

3.3.4 Relative Humidity Cycling Profile

To generate cyclic loading on the membranes, a relative humidity (RH) cycling test, developed by WL GoreTM [121] to assess the mechanical durability of the membrane in the absence of chemical reactions, is used. It is a similar testing protocol to the one used in the experiments by Lai et al. [87]. The cycling test consists of heating the fuel cell to 80 °C and forcing saturated air at 80 °C and 100% RH through the flow channels on both the anode and cathode side of the MEA for 10s, followed by forcing dry air at 80 °C and 30% RH for 50s. This cycling test is simulated in the

finite element models by applying the following boundary conditions on the channel regions as illustrated in Figure 3-4:

1. Initial condition: The entire model is subjected to a uniform temperature of 25 °C and relative humidity (RH) of 30%. The water volume fraction, ϕ_w , corresponding to 30% RH is 0.06 [54,76].
2. Hydration: The temperature of the cell is increased to 80 °C and the RH at the surface of gas diffusion layer (GDL) is increased to 100% over 1s at a constant rate. The water volume fraction, ϕ_w , corresponding to 100% RH is 0.32 [54,76] and is held for 10s, while the temperature is held at 80 °C for the rest of the simulation.
3. Dehydration: At T = 80 °C, the RH at the surface of GDL is decreased to 30% over 1s and kept for 50s, meaning the water volume fraction, ϕ_w , is reduced to 0.06.

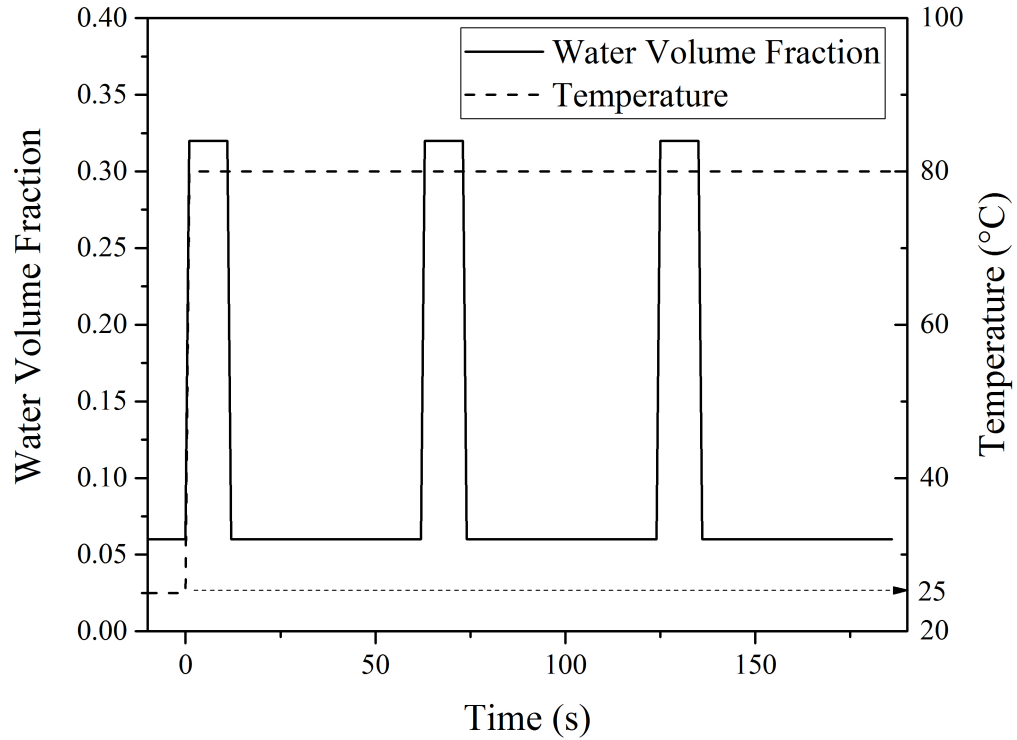


Figure 3-4 Profile of humidity cycling test used in simulations.

3.3.5 Solution Procedures

In the WL GoreTM RH cycle described above, humid and dry air is alternately forced into the flow channels and is modeled as alternating boundary conditions on the exposed gas diffusion layer (GDL) surfaces in the channel areas [53,54,70,76]. In the case of humid air, the humid air acts as a constant water source and water diffuses through the GDLs and electrodes into the membrane, which hydrates the membrane. In the case of dry air, the dry air acts as a water sink and water diffuses from the membrane through the electrodes and GDLs into the water sink, which dehydrates the membrane. In this work, only water diffusion is considered to determine the water

profile, and the time-dependent water profile in the membrane is determined by the water diffusion through the channel boundaries, GDLs, electrodes and the membrane itself [53,54,70,76]. Therefore, compared with the applied water volume fraction at the flow channel boundaries, the water volume fraction in the membrane has a time-lag, as is illustrated in Figure 3-5 [54,76].

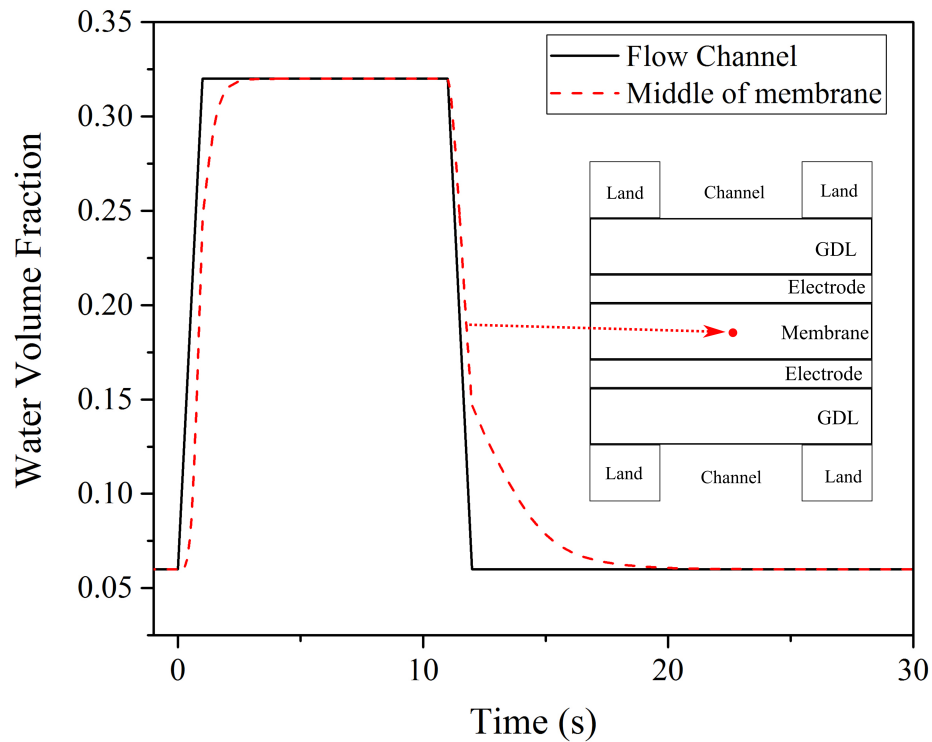


Figure 3-5 Water volume fraction variation at the flow channel boundaries and at the middle of the membrane

The water volume fraction determines the swelling strain due to water uptake, and the materials properties of the PFSA membrane are strongly dependent on the water volume fraction of the membrane, both of which will affect the stress/displacement fields [53,54,70,76]. The stress/displacement fields will, in turn, limit the swelling strain and consequently affect the water volume fraction profile in the membrane [53,54,70,76]. Therefore, the water volume fraction and the stress/displacement fields are coupled, and the water volume fraction for each node is modeled as a third degree of freedom in addition to the two nodal displacements in the finite element model [53,54,70,76]. A coupled water-volume-fraction-displacement analysis is conducted to simultaneously solve the water volume fraction and stress/displacement fields [53,54,70,76].

Even though ABAQUS does not have a specific analysis procedure for water diffusion, this process follows the same governing equations as heat conduction and swelling strains have the same characteristics as thermal strains. Therefore, the coupled temperature-displacement analysis procedure in ABAQUS [102] is modified to solve the coupled water-volume-fraction-displacement problem with temperature in ABAQUS representing the water volume fraction in this work. An additional field value is created in ABAQUS to represent the temperature in this work. CPE4RT elements in ABAQUS [102], which are 4-node bilinear coupled temperature-displacement plane strain elements with three active degrees of freedom (x displacement, y displacement and temperature (as a proxy for water content)), are used in finite element models.

3.3.6 Mesh Convergence

The accumulation of plastically dissipated energy is compared to a critical value to determine crack growth, so the accumulation of plastically dissipated energy in a domain of fixed area ($30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$) is tracked across four different mesh sizes ($0.3\text{ }\mu\text{m}$, $0.25\text{ }\mu\text{m}$, $0.2\text{ }\mu\text{m}$ and $0.15\text{ }\mu\text{m}$) in the structurally refined mesh area at the crack tip. Results are plotted in Figure 3-6.

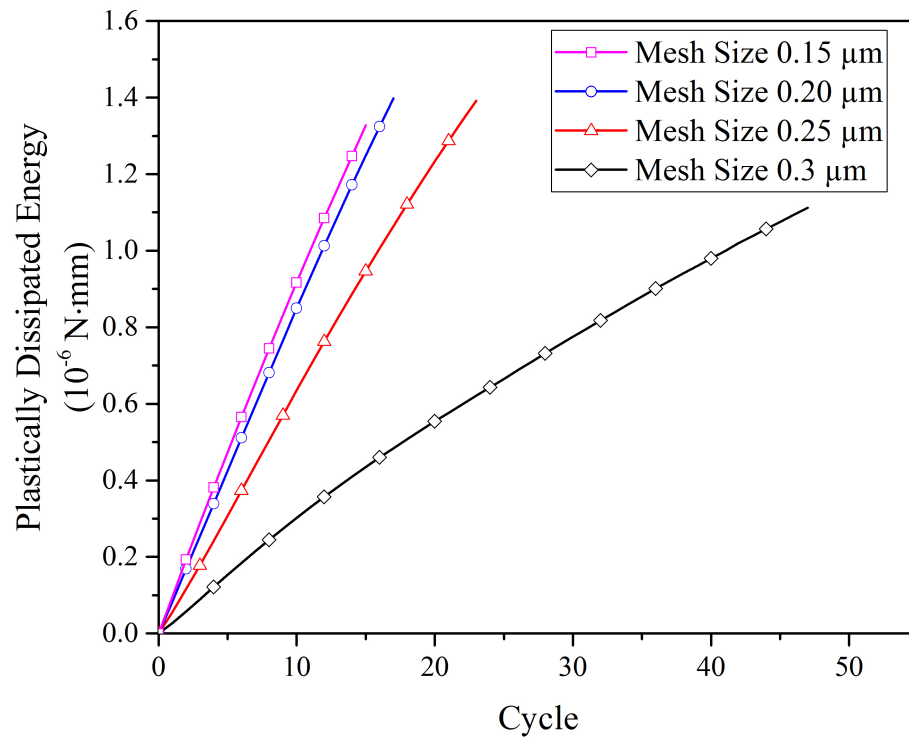


Figure 3-6 Accumulation of plastically dissipated energy as a function of relative humidity (RH) cycles among four different mesh sizes in the structurally refined mesh area at crack tip.

From Figure 3-6, the accumulation of plastically dissipated energy for the same-sized dissipation domain differs by about 6% between mesh sizes of 0.2 μm and 0.15 μm , indicating fairly good convergence at this level of refinement.

Figure 3-7 shows the crack length into the membrane as a function of the number of relative humidity (RH) cycles for the coarser 0.2 μm and the finer 0.15 μm mesh. The average crack growth rate for the 0.2 μm mesh is about 0.0158 $\mu\text{m}/\text{cycle}$, while the average crack growth rate for the 0.15 μm mesh is about 0.0171 $\mu\text{m}/\text{cycle}$, differing only about 8%, further indicating mesh convergence.

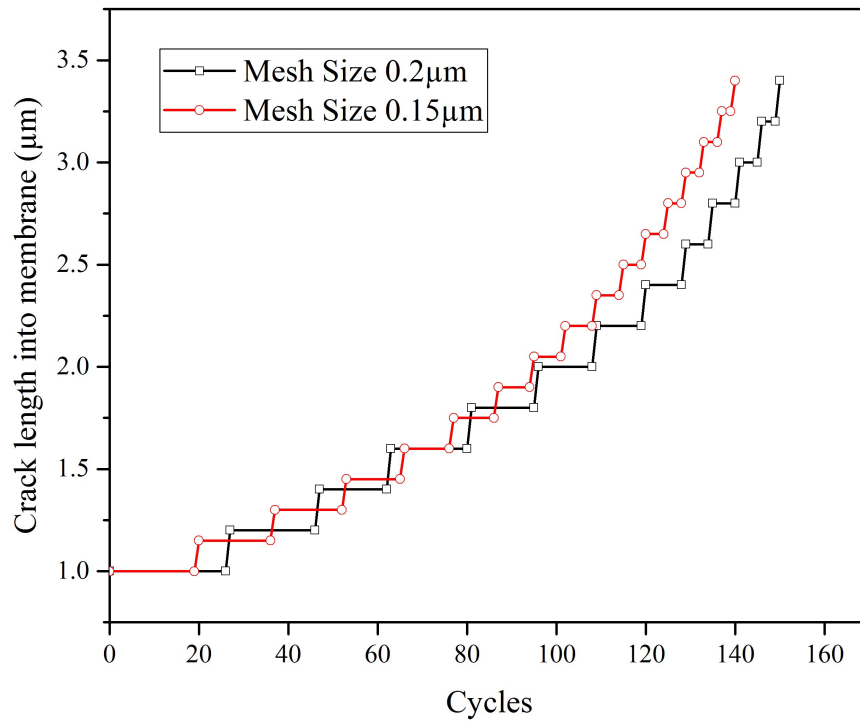


Figure 3-7 Propagated crack length into membrane as a function of the number of relative humidity (RH) cycles for two different mesh sizes.

Based on these results, the structurally refined mesh along the crack path in the following sections is composed of a uniform array of square isoparametric quadratic CPE4RT elements [102] with size 0.2 μm by 0.2 μm . This mesh size also allows for crack growth through a significant portion of the membrane thickness during the simulation. Using this mesh, the crack propagates in increments of 0.2 μm each time the accumulation of plastically dissipated energy, ΔW^p , in the dissipation domain reaches the critical value of plastically dissipated energy, W_{cr}^p .

3.3.7 Dissipation Domain

In References [19,43], during the loading cycle, the material ahead of the crack tip yields in tension because of the stress concentration induced by the crack. This forms a region known as the forward plastic zone [19,43]. Due to the permanent deformation associated with this yielding, compressive stresses are introduced during unloading and therefore compressive yielding typically develops in a smaller region known as the reverse plastic zone [19,43]. As the structure is continuously cycled, the material within the reverse plastic zone undergoes forward and reverse yielding and there is continuous accumulation of plastically dissipated energy [19,43]. Therefore, the reverse plastic zone is chosen as the dissipation domain in [19,43], and the size is approximated by analysis based on References [4,9].

Previous simulations show that under typical fuel cell loading conditions, the entire PFSA membrane yields [68-71]. Therefore, plastic energy is dissipated throughout the membrane during any particular load cycle and there is no such distinct forward plastic zone or reverse plastic zone in the PFSA membrane. However, preliminary studies of a cracked membrane showed that there is significantly greater accumulation of plastically dissipated energy near the crack tip. Therefore, to create a

robust simulation, it is postulated here that the dissipation domain should encompass a region around the crack tip where the accumulation of plastically dissipated energy is significantly greater than the average increase in the membrane after a few RH cycles. The following scheme is used to determine the appropriate dissipation domain size in this work.

First, the plastically dissipated energy density in a typical element far away from the crack tip (the crack length is 13 μm) is calculated. The ratio of the plastically dissipated energy density in each element near the crack tip to that in the element far away from the crack tip is calculated. To account for angular variations, elements along three representative angles, 0° , 45° and 90° , are chosen as illustrated in Figure 3-8. The elements are all of the same size of 0.2 μm by 0.2 μm (based on the convergence study discussed previously). The first element in front of the crack tip (Element 0) is chosen as the origin. An element-wise distance is defined as the number of elements away from the origin along each angle. Thus, Elements 1^0 , labeled in Figure 3-8, has an element-wise distance of 1, while the element next to it along 0° will have an element-wise distance of 2. The same element-wise distances are defined along 45° and 90° .

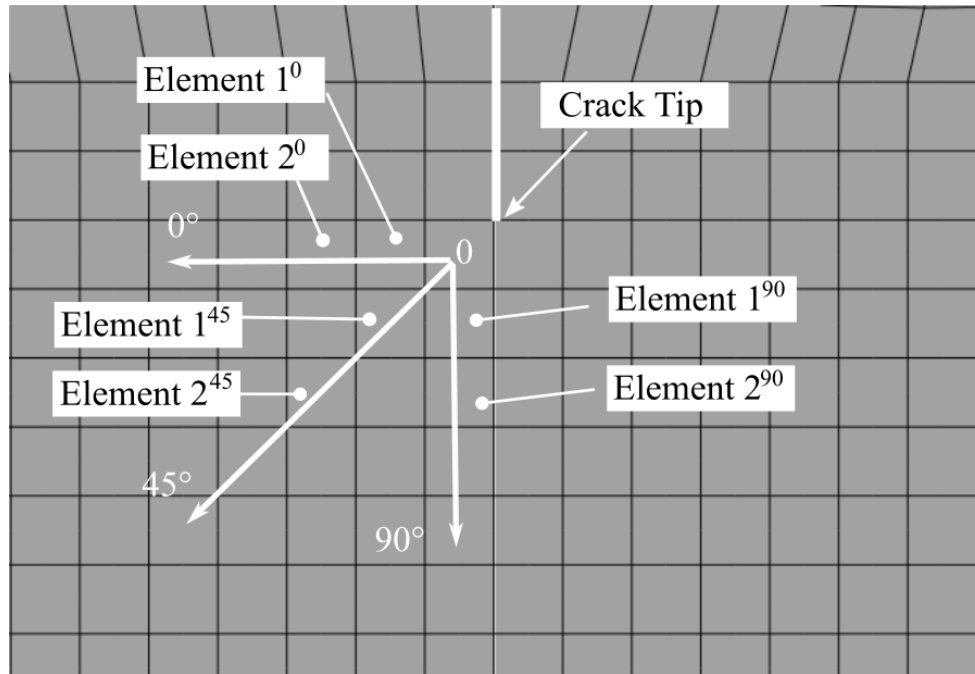


Figure 3-8 Numbering scheme for elements along different angel in the structurally refined mesh area at the crack tip

The ratio of the plastically dissipated energy density in each element near the crack tip to that in the element far away from the crack tip, as a function of element-wise distance along different angle, is plotted in Figure 3-9. Figure 3-9 shows that element 0 has a very high ratio of about 341. However, as elements farther away from the crack tip are selected, the ratio drops significantly. For an element-wise distance of 7, the ratio is very close to 1, meaning that the plastically dissipated energy density in this element is close to the far-field value.

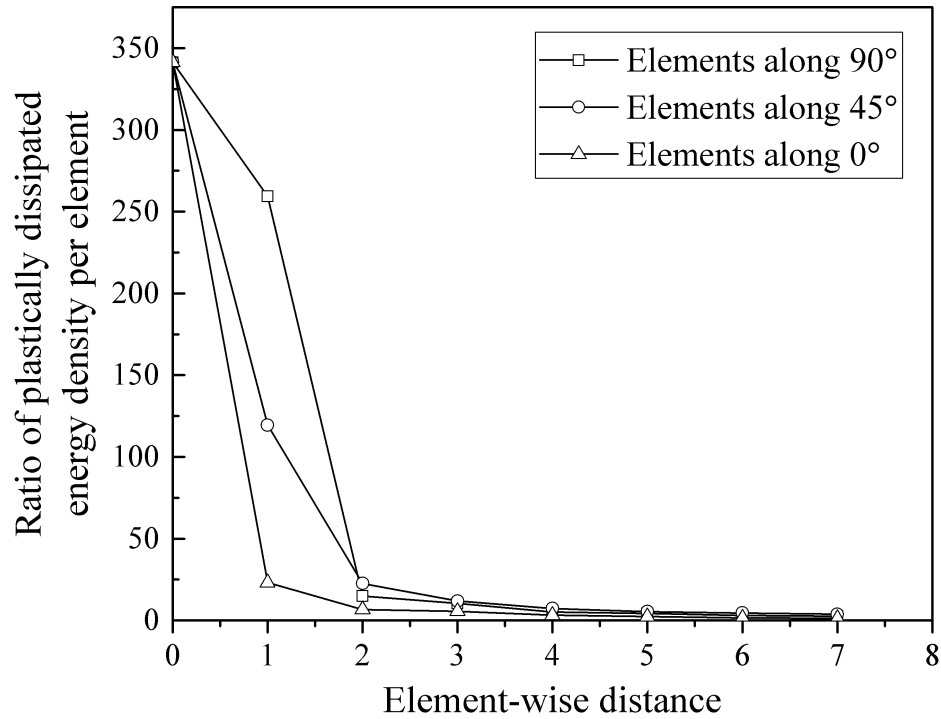


Figure 3-9 Ratio of plastically dissipated energy density per element as a function of the element-wise distances as defined in Figure 3-8.

In this qualitative study, a constant dissipation domain is used through the simulation to investigate the use of plastically dissipated energy as a criterion to study the general experimental observations. Therefore, the dissipation domain in the simulation is selected as an 8 by 8 element rectangular domain on either side of the crack (1.6 μm by 1.6 μm square domain). This dissipation domain is able to capture the majority of the plastically dissipated energy increment around the crack tip, without having that increment obscured by the increase in plastically dissipated energy in the rest of the membrane.

3.3.8 The Critical Value of Plastically Dissipated Energy W_{cr}^p

The critical value of plastically dissipated energy, W_{cr}^p , is assumed to be a material property that needs to be determined from experiments. However, to the knowledge of the author, no such values are available in the open literature for unreinforced PFSA or ePTFE reinforced PFSA. Therefore, for this study, the value is assumed to be $2.0\text{E-}6 \text{ N}\cdot\text{mm}$ for both unreinforced PFSA and ePTFE reinforced PFSA. This choice is made to achieve crack propagation rates that allow the simulations to run for several hundred cycles. The following results are intended to demonstrate that the concepts and implementation give qualitatively meaningful results, but the numbers are not intended to be quantitatively accurate.

3.4 Results and Discussions

3.4.1 Crack Propagation in Unreinforced PFSA Membrane

As a first example and a baseline for comparison, crack propagation at the center of the channel in an unreinforced PFSA membrane is investigated. The membrane is subjected to the relative humidity (RH) cycling protocol described in Section 3.3.4. Figure 3-10 (solid line marked with squares) shows the crack length into the membrane as a function of the number of cycles. Note that the crack propagation is based on the scheme described in Section 3.2.2 and the result is a direct output from the simulation based on the plastically dissipated energy criterion. Propagation is not prescribed beforehand. Since the initial crack length is $13 \mu\text{m}$ and the electrode is $12 \mu\text{m}$ thick, the initial value of crack length into the membrane is $1 \mu\text{m}$. When the crack propagates by $5.6 \mu\text{m}$ (the crack length into the membrane reaches $6.6 \mu\text{m}$), the simulation is stopped due to convergence and computational time issues. As is mentioned in Section 3.3.6, the structurally refined mesh through which the crack

propagates is composed of a uniform array of square isoparametric quadratic CPE4RT elements with size $0.2\ \mu\text{m}$ by $0.2\ \mu\text{m}$. With the scheme illustrated in Figure 3-1, the crack propagates by $0.2\ \mu\text{m}$ each time the plastically dissipated energy in the dissipation domain reaches the preset critical value. Therefore, a total of 28 elements are released during the simulation.

Initially, the plastically dissipated energy accumulates at a low rate per cycle and it takes about 26 RH cycles before it reaches the critical value of plastically dissipated energy for the first time. As the crack grows, the plastically dissipated energy accumulates at a slightly higher rate. In addition, there is already plastic deformation in the region around the crack tip region, which also affects the mechanics and the accumulation of plastically dissipated energy. Therefore, it takes about 19 RH cycles before the second propagation increment of the crack. Subsequently, the plastically dissipated energy accumulates at a higher rate, so the crack propagates at an increasingly higher rate. The period prior to the initial propagation increment contains the majority of the useful membrane life in this case.

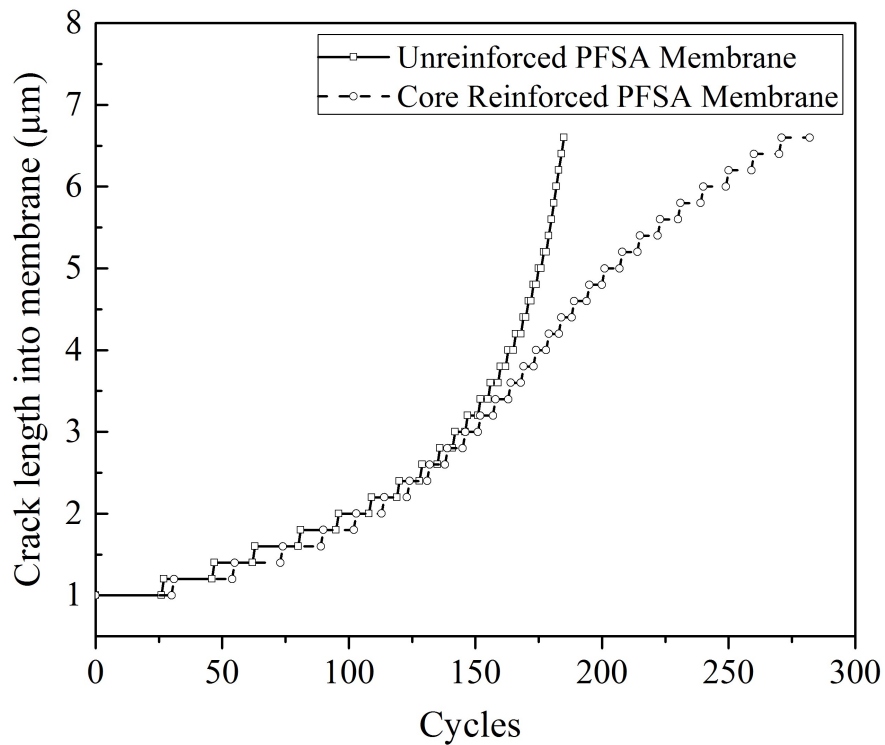


Figure 3-10 Crack propagation in unreinforced PFSA membrane and core reinforced PFSA membrane.

As discussed previously, Lai et al. [87] conducted similar humidity cycling tests on Nafion[®] NR111 membranes (25 μm thick unreinforced PFSA membranes) and showed the morphology of cracks at various stages of growth using cross-sectional micrographs. These are illustrated in Figure 1-5(a) and 1-5(b). The micrographs show that initially when the crack is short, it is relatively sharp and blunts as it grows. This is qualitatively captured by the simulation as can be seen from “snapshots” of the model taken at the beginning and end of the simulation (Figure 3-11(a) and 3-11(b)). It is worth pointing out that in the experiment, the MEA was

sandwiched between two GDLs by clamping and it may have been possible for the electrode surfaces to slip relative to the GDLs during hydration and dehydration. In the simulation, however, perfect bonding between the electrodes and GDLs was assumed. Also, to obtain the micrographs in Figure 1-5, Lai et al. [87] disassembled the fuel cells. These factors may explain why in the later stages of crack growth, the electrodes from the simulations look different than those in the experiments.

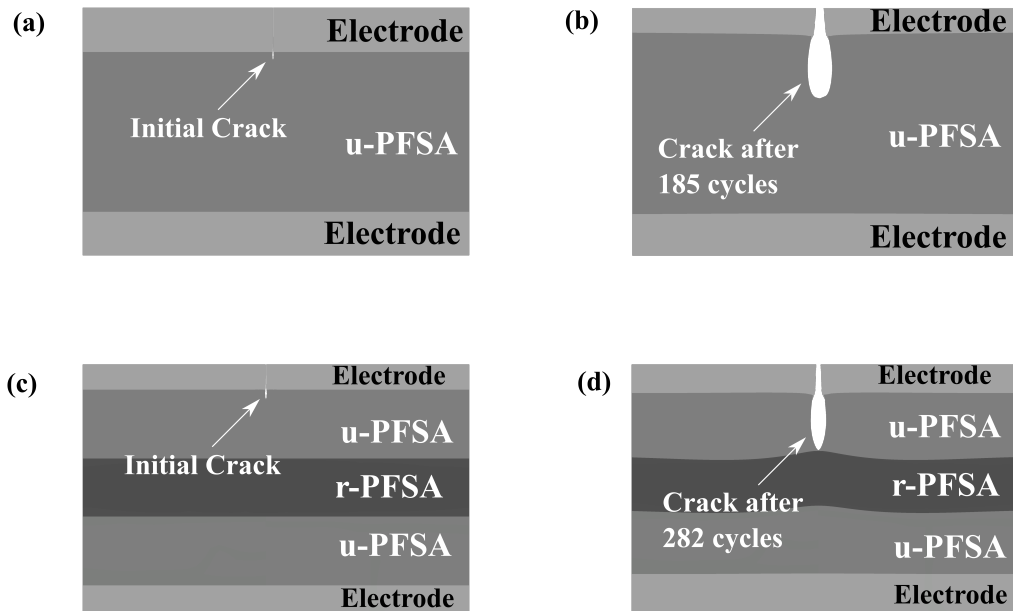


Figure 3-11 Crack morphology of unreinforced PFSA membrane and core reinforced PFSA membrane from simulation snapshots. (a) Initial crack opening morphology of unreinforced PFSA membrane, (b) Crack opening morphology of unreinforced PFSA membrane after 185 relative humidity cycles, (c) Initial crack opening morphology of core reinforced PFSA membrane, (d) Crack opening morphology of core reinforced PFSA membrane after 282 relative humidity cycles.

3.4.2 Crack Propagation in Core Reinforced PFSA Membrane

To improve mechanical durability, PFSA membranes using reinforcing agents such as polyvinylidene fluoride, expanded polytetrafluoroethylene (ePTFE) fibrils and other polymers have been developed [122-127]. In particular, WL GoreTM has developed the Gore-Select[®] membrane, which is a three-layer composite membrane consisting of two layers of unreinforced PFSA on either side of a layer of ePTFE reinforced PFSA. Gore[®] Primea[®] §Membrane Electrode Assembly (MEA), is the Gore-Select[®] membrane coated with catalyst electrodes. Gittleman et al. [59] conducted RH cycling tests on MEAs with Nafion[®] NRE211 membranes (unreinforced PFSA membrane) and Gore[®] Primea[®] Series 57. After RH cycling tests, through-thickness cracks were found in the membrane thickness direction of Nafion[®] NRE211 membrane while in the Gore[®] Primea[®] Series 57 MEA, the reinforcement improved the resistance against the crack propagation in the thickness direction. By measuring the H₂ crossover, Liu et al. [128] studied the lifetime of various PEM fuel cell membranes and found that the ePTFE reinforcement increased the lifetime. Li et al. [79] conducted biaxial cyclic loading test on various PEM fuel cell membranes using pressure-loaded blisters, and found that the ePTFE reinforcement delayed the formation of cracks and crazes. Lai et al. [87] showed that compared with Nafion[®] NRE111 membranes, Gore-Select[®] 57 membranes had improved lifetime under RH cycling tests. A number of other studies [60,82,129-131] have reported increased durability with ePTFE reinforced PFSA membranes. This increased durability is generally attributed to the observations that ePTFE reinforcement improves the dimensional stability and increases the in-plane strength of the membrane, both

§ Gore[®] Primea[®] is a registered trademark of W.L. Gore Inc.

favorable for reducing the probability of failure, such as pinhole growth or crack formation [61,71,128,132].

The morphology of cracks at various stages of growth in Gore-Select[®] 57 membranes (core reinforced PFSA membranes) from the RH cycling experiment test conducted by Lai et al. [87] are shown Figure 1-5(d) and 1-5(e). Crack morphologies from the simulations of reinforced membranes are shown in Figure 3-11(c) and 3-11(d). From the experiment micrographs (Figure 1-5(d) and 1-5(e)), similar to the crack in the unreinforced PFSA membranes (Figure 1-5(a) and 1-5(b)), the initial crack is relatively sharp and as it propagates the crack tip becomes blunted. Also apparent from Figure 1-5(d) and 1-5(e) is that the initially flat reinforcement layer has become wavy in the out-of-plane direction. As seen in Figure 3-11(c) and 3-11(d), the simulation captures the crack propagation, the blunting of the crack tip, and the waviness in the ePTFE reinforced PFSA layer after humidity cycling. All of these features are directly obtained by probing the plastically dissipated energy in the dissipation domain ahead the crack-tip, assessing it as a criterion for crack propagation and propagating the crack via a node-release scheme once the criterion is satisfied.

Figure 3-10 shows the crack length as a function of the number of cycles in the simulations for both the unreinforced PFSA membrane and core reinforced PFSA membrane. Since the core reinforced PFSA membrane has unreinforced PFSA as the outer layers, the initial crack propagation behavior in a core reinforced PFSA membrane is similar to the case of crack propagation in an unreinforced PFSA membrane. Initially, the crack grows slowly and as the crack becomes longer it grows faster. However, in the core reinforced PFSA membrane, as the crack propagates towards the ePTFE reinforcement (corresponding to the point where the crack length

into membrane is 7 μm in Figure 3-10), the influence of the ePTFE reinforcement becomes significant. The accumulation rate of plastically dissipated energy slows down and it takes more cycles for the plastically dissipated energy to reach the critical value. As a result, the crack propagation in a core reinforced membrane slows down. After about 185 cycles, the crack in an unreinforced PFSA membrane has grown from 1 μm to 6.6 μm and it appears that it will only take a few more cycles before the crack grows through the thickness. However, the crack in a core reinforced PFSA membrane only grows from 1 μm to 4.4 μm after the same number of cycles. In total, it takes about 282 cycles before the crack in a core reinforced PFSA membrane reaches 6.6 μm . As is stated in Section 3.3.2, in this study the crack has not reached the interface of PFSA membrane and ePTFE reinforcement. It is possible that after the crack reaches the interface, it will continue to grow through thickness or it may grow along the interface. This is not investigated in the current study since the critical values of plastically dissipated energy, W_{cr}^p , is unknown for either the unreinforced or the reinforced membrane or the interface between them. Compared with an unreinforced PFSA membrane, a core reinforced PFSA membrane has improved life time under RH cycling tests. Therefore, the influence of the reinforcement on fatigue crack growth is qualitatively captured by the simulation based on the plastically dissipated energy criterion.

3.4.3 Crack Propagation in Unreinforced PFSA Membrane under Channel and under Land

In cyclical RH experiments, as well as in actual PEM fuel cells, failures in the form of cracks and pinholes in the membrane are more commonly found in the regions under the flow channels than under the lands [58,59,79,87,133,134]. In this section,

the ability of the plastically dissipated energy criterion to capture this observation is studied. For this, a second finite element model containing MEA with unreinforced PFSA membrane is created to have a full land and two half channels (Figure 3-3). An initial crack of the length 13 μm is assumed in the model with the crack under the land region. Propagation of the crack under the land is tracked and compared with propagation of the crack under the channel from the previous model (Figure 3-2).

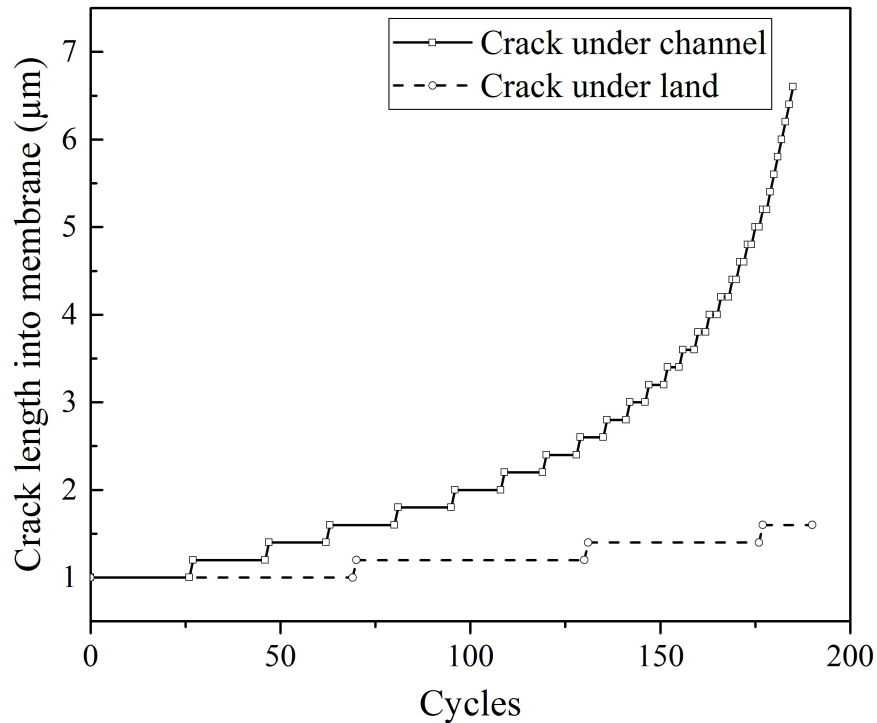


Figure 3-12 Propagation of a crack under channel region and a crack under land region.

Figure 3-12 shows that the crack under the channel propagates much faster than the crack under the land. When the crack under the channel has reached a length of 6.6 μm into the membrane, the crack under the land is just 1.6 μm . After a relatively few more humidity cycles, the crack under the channel will likely develop into a through-thickness crack, while the crack under the land will still be relatively short. Therefore, if initial flaws (e.g. the 13 μm pre-cracks modeled here) are equally likely in the channel and land regions, then critical flaws are far more likely to develop in the channel regions. These findings agree with the experimental and in-field observations that through-thickness membrane cracks are generally only found under the channel regions and not under the land regions.

3.4.4 Crack Propagation in Unreinforced PFSA Membrane under Different Clamping Loads

Within certain limits, increased clamping load has been observed to have a positive effect on the mechanical durability of the membranes [135]. In this section, the effect of clamping load on crack propagation in the membrane is investigated using simulations. Within the framework of the models used here, clamping is controlled by fixing the vertical displacement of the upper surface in the FE model at ambient conditions and holding constant. The swelling expansion of the membrane, therefore, increases the clamping load during the hygrothermal loading in the simulations. Three selected ambient clamping displacement conditions are studied: 0.0 mm, 0.05 mm and 0.1 mm. Larger clamping displacements correspond to higher clamping loads being applied during fuel cell stack assembly.

Crack propagation under the selected clamping conditions is shown in Figure 3-13. For the case where a 0.0 mm clamping displacement is applied (the baseline case

discussed in Section 3.4.1 and repeated here for clarity) after about 185 cycles, the crack has grown by 5.6 μm (the crack length into the membrane is 6.6 μm). However, when a 0.05 mm clamping displacement is applied, after 185 cycles the crack has grown only by 1.6 μm (the crack length into the membrane is 2.6 μm). It takes a total of about 259 cycles before this crack propagates by 5.6 μm (the crack length into the membrane is 6.6 μm). For the case of clamping displacement 0.1 mm, the crack has only grown by 1.2 μm (the crack length into the membrane is 2.2 μm) after 335 cycles. Further simulation was not conducted in the case of 0.1 mm clamping because of the computation time involved. In summary, fatigue crack simulation based on the plastically dissipated energy criterion agrees qualitatively with observations from experiments, suggesting that increased clamping pressure reduces the crack propagation rate, thus increasing the durability of membrane.

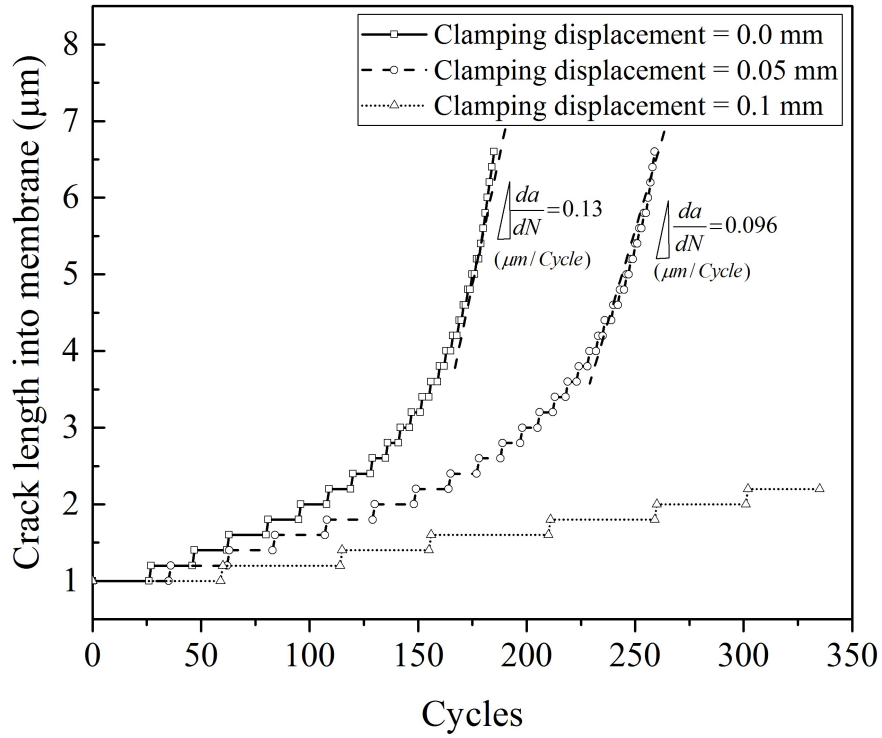


Figure 3-13 Crack propagation in unreinforced PFSA membrane under different clamping displacements.

3.4.5 Crack Propagation in Unreinforced PFSA Membrane under Different Relative Humidity Cycling Profiles

Experimental results show that longer holding times in relative humidity (RH) cycling result in a smaller number of cycles to failure under RH cycling tests. In this section, the effect of different RH cycling profiles on the number of cycles to failure is investigated using the plastically dissipated energy criterion.

A different RH cycling profile developed by the U.S. Department of Energy (DoE) [136] is implemented into the finite element model. This RH cycling profile is similar to the GoreTM RH cycling profile introduced in Section 3.3.4, but with

different holding times. In the DoE cycle, the fuel cell is kept hydrated for 120s after hydration instead of 10s and kept dehydrated for 120s after dehydration instead of 50s. This cycling test is illustrated in Figure 3-14.

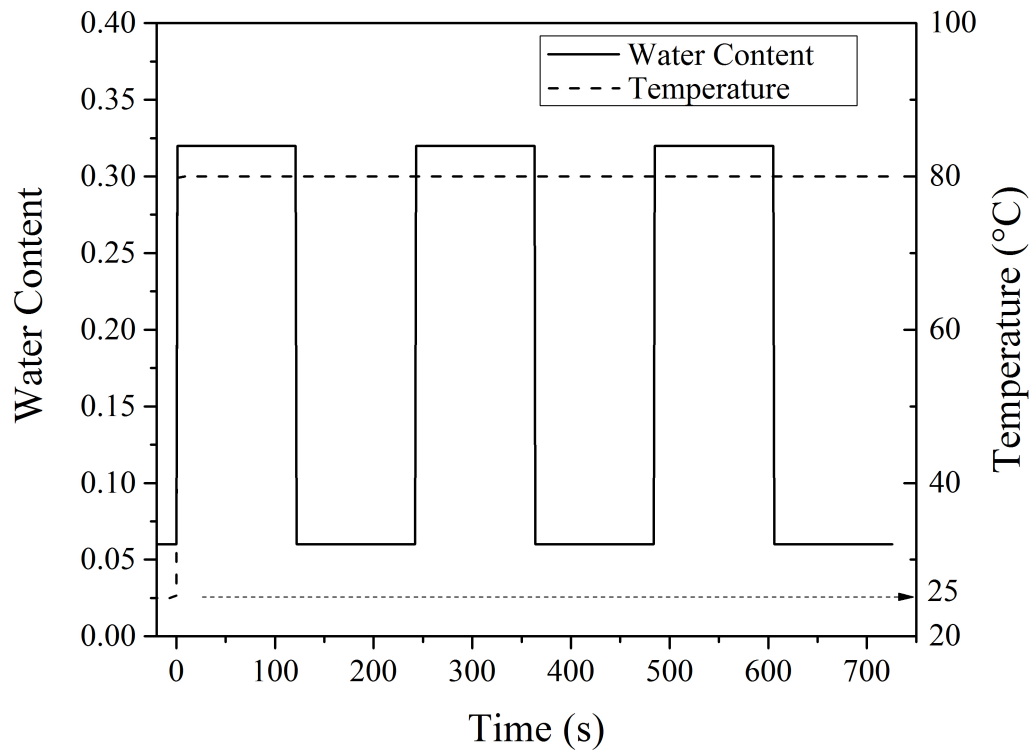


Figure 3-14 Profile of the DoE humidity cycling test [136]

Crack propagation under the two different RH cycling profiles (GoreTM cycle in Figure 3-4 and DoE cycle in Figure 3-14) is shown in Figure 3-15. For the case where DoE RH cycling (longer holding time after hydration and dehydration) is applied, after about 79 cycles, the crack has grown by 5.8 μm (the crack length into

the membrane is 6.8 μm). However, for the case where GoreTM RH cycling (shorter holding time after hydration and dehydration) is applied (the baseline case discussed in Section 3.4.1 and repeated here for clarity) after 79 cycles, the crack has grown only by 0.6 μm (the crack length into the membrane is 1.6 μm). It takes a total of about 185 cycles before this crack propagates by 5.6 μm (the crack length into the membrane is 6.6 μm). Therefore, the DoE RH cycling will result in a smaller number of cycles to failure than the GoreTM RH cycling. In summary, fatigue crack simulation based on the plastically dissipated energy criterion agrees qualitatively with observations from experiments that longer holding time after dehydration and hydration in RH cycling test leads to a smaller number of cycles to failure under RH cycling tests.

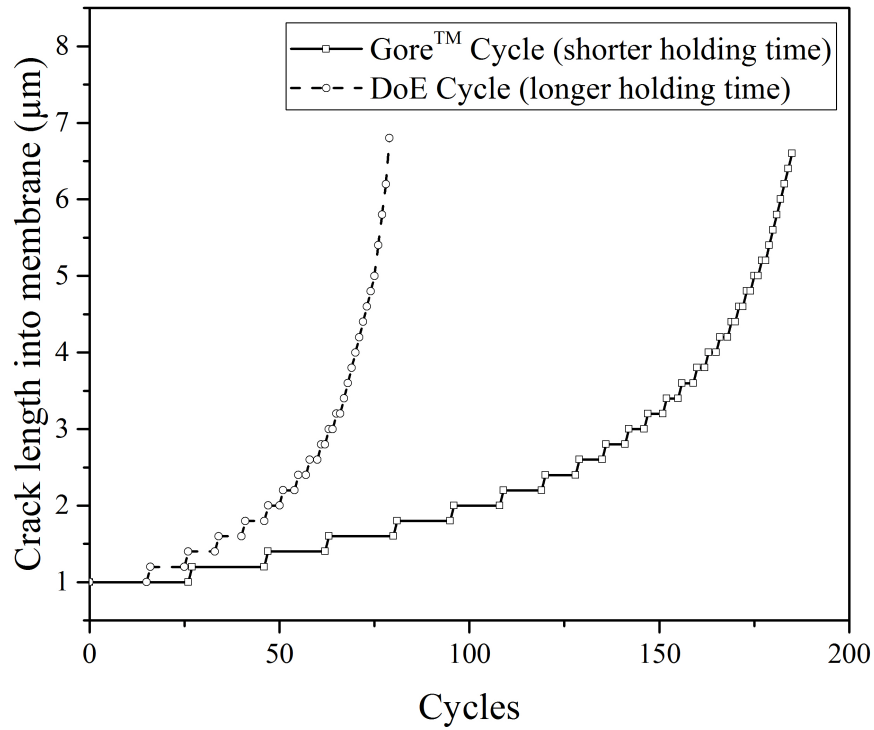


Figure 3-15 Crack propagation in unreinforced PFSA membrane under different RH cycling profiles.

3.5 Synopsis

There are several original contributions to the literature made in this chapter. First, the plastically dissipated energy criterion algorithm developed by Cojocaru and Karlsson [43] and Nittur et al. [19] has been extended to account for crack propagation in situations where the plastic deformation extends throughout the structure. Secondly, this chapter shows this extended algorithm is useful for studying fatigue crack growth

in PEM fuel cell membranes under relative humidity (RH) cycling. To the author's knowledge, this is the first attempt to model *in-situ* crack-propagation in the polymer electrolyte membrane during cyclical hygrothermal loading, using time-dependent visco-plastic membrane mechanical properties. Thirdly, the work in this chapter qualitatively captures a number of observed phenomena related to the durability of PEM fuel cell membranes both *in-situ* and in experiments. In this work, the accumulation of plastically dissipated energy in the dissipation domain at the crack tip is compared with a preset critical value, which is assumed to be an as-yet undetermined material property. Once the critical value of plastically dissipated energy is determined, crack growth rates can be obtained directly from this simulation and could be used to make lifetime predictions of various membranes under a variety of loading conditions.

Crack propagation in PEM fuel cell membranes under RH cycling was simulated in two-dimensional representative PEM fuel cell models created in the commercial finite element package ABAQUS. It is well-established experimentally that during RH cycling, the crack tip will blunt and that ePTFE reinforced PSFA membranes offer better durability than unreinforced PFSA membranes. From experimental and in field observations, through-thickness membrane cracks are generally found under the channel regions but not under the land regions, and within certain limits, increasing clamping on the fuel cell improves the mechanical durability of the membrane. In addition, data provided by W.L. Gore shows that the number of RH cycles to failure depends on the hold time at the saturated and dry conditions, with the longer hold time at saturated and dry conditions leading to a smaller number of cycles to failure. These conditions were all investigated within the context of the finite

element model developed here and the proposed plastically dissipated energy criterion captured all of these observations qualitatively. Thus, the proposed numerical scheme, with a plastically dissipated energy criterion, may be a useful tool to numerically characterize crack propagation in PEM fuel cell membranes under RH cycling. The possibility exists of expanding the methodology to simulate other materials, other fuel cell designs and a wider range of loading conditions (including field operation).

The critical value of dissipated plastic energy is assumed to be a material property, and can therefore only be determined from experiments. Values for this material property for PFSA membranes are as-yet undetermined. In the current investigation, it is given an assumed value to obtain reasonable overall simulation times and to test the viability of the proposed methodology. The results above are intended to demonstrate that the concepts and implementation of plastically dissipated energy criterion give qualitatively meaningful results, but the numbers are not intended to be quantitatively accurate.

Calibration and further development of the proposed plastically dissipated energy criterion will require experimental measurements. Once the critical value of plastically dissipated energy is determined from experiments, it can be implemented into the model to provide more quantitatively meaningful results. The next chapter focuses on establishing the critical value of plastically dissipated energy for PFSA membrane.

Chapter 4

ESTABLISHING THE CRITICAL VALUE OF PLASTICALLY DISSIPATED ENERGY FOR PFSA MEMBRANE

4.1 Introduction

So far, it has been shown that plastically dissipated energy can be used to quantitatively predict fatigue crack growth in a range of polymers, and it has also been shown that plastically dissipated energy can qualitatively capture the fatigue crack growth behavior in PEM fuel cell membranes under relative humidity (RH) cycling. Central to this hypothesis is that the critical value of plastically dissipated energy is assumed to be a material property that needs to be determined from experiments. In Chapter 2, the critical value of plastically dissipated energy for several polymers was determined using the method proposed in Nittur et al. [19] by matching an experiment data point with a simulation point. However, to the knowledge of the author, no such values are available in open literature for PFSA or ePTFE reinforced PFSA. Therefore, in Chapter 3, the critical value of plastically dissipated energy was selected so to obtain reasonable overall simulation times and to test the viability of the proposed methodology.

In this chapter, efforts made to determine the critical value of plastically dissipated energy for unreinforced PFSA are discussed. First, *ex-situ* mechanical fatigue tests are conducted at different combination of temperatures, relative humidity (RH) and mean loads, and the numbers of cycles to failure are recorded for each case. Then, finite element simulations are conducted to determine the critical value of

plastically dissipated energy for the unreinforced PFSA using the iterative framework illustrated in Figure 4-1.

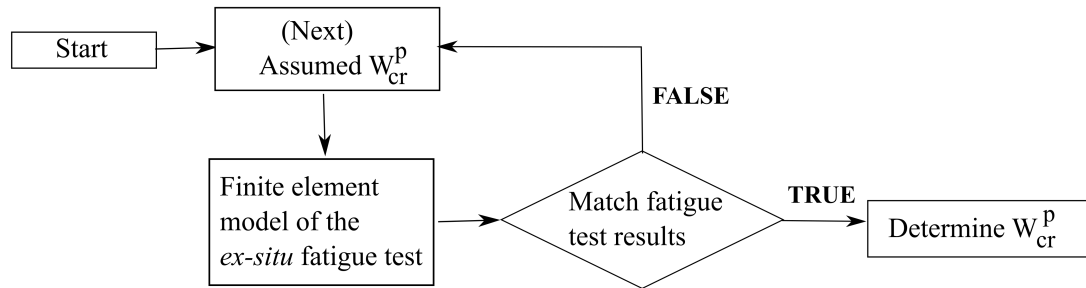


Figure 4-1 Flow chart of the iterative algorithm for determining the critical value of plastically dissipated energy.

4.2 Experiment Procedures and Results

The *ex-situ* mechanical fatigue tests were conducted at the University of Delaware by Jun Qian [137]. The test equipment, conditions and procedure are described briefly here.

The tests were conducted using an MTS[®] 858 Mini Bionix[®] II material testing system with an ESPEC[®] environmental chamber as illustrated in Figure 4-2. The ESPEC[®] environmental chamber is able to maintain the desired temperature and relative humidity (RH) for testing.

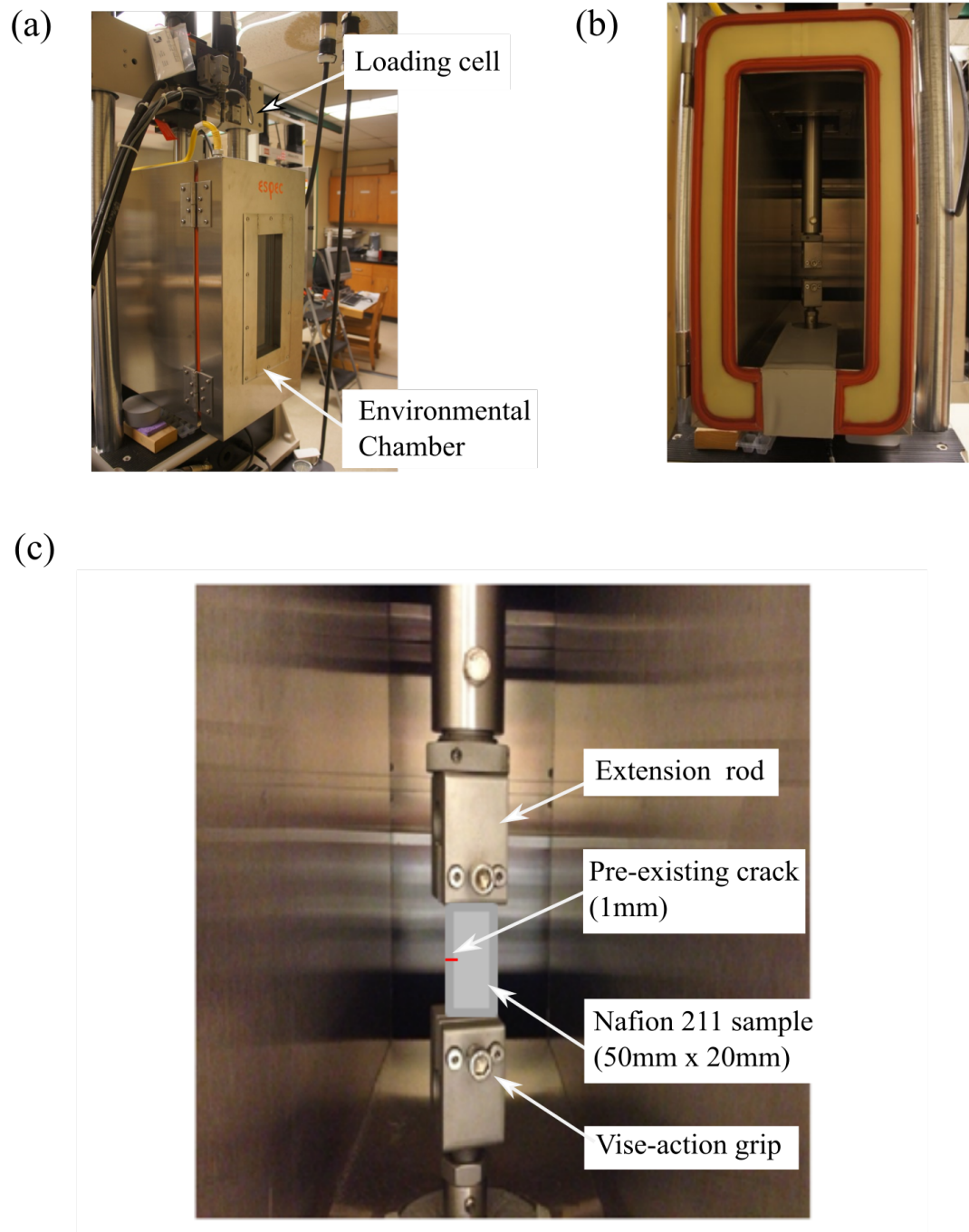


Figure 4-2 (a) MTS[®] 858 Mini Bionix[®] II material testing system with an ESPEC[®] environmental chamber; (b) ESPEC[®] environmental chamber; (c) Experimental setup.

The test samples (Nafion[®] 211 membranes) were prepared in rectangular shape of 20 mm by 50 mm. An edge crack of 1 mm is introduced in the middle of the membrane using a liquid nitrogen chilled blade to ensure the sharpness of the crack, as is illustrated in Figure 4-2.

To avoid the membrane going slack during fatigue testing, the test sample was loaded using positive (tensile) minimum and maximum loads at 0.1 Hz using a sine wave load-controlled loading profile. The load amplitude was set at 4.8 MPa and three different mean loads, 4.0 MPa, 4.4 MPa and 4.8 MPa, were investigated, as is illustrated in Figure 4-3.

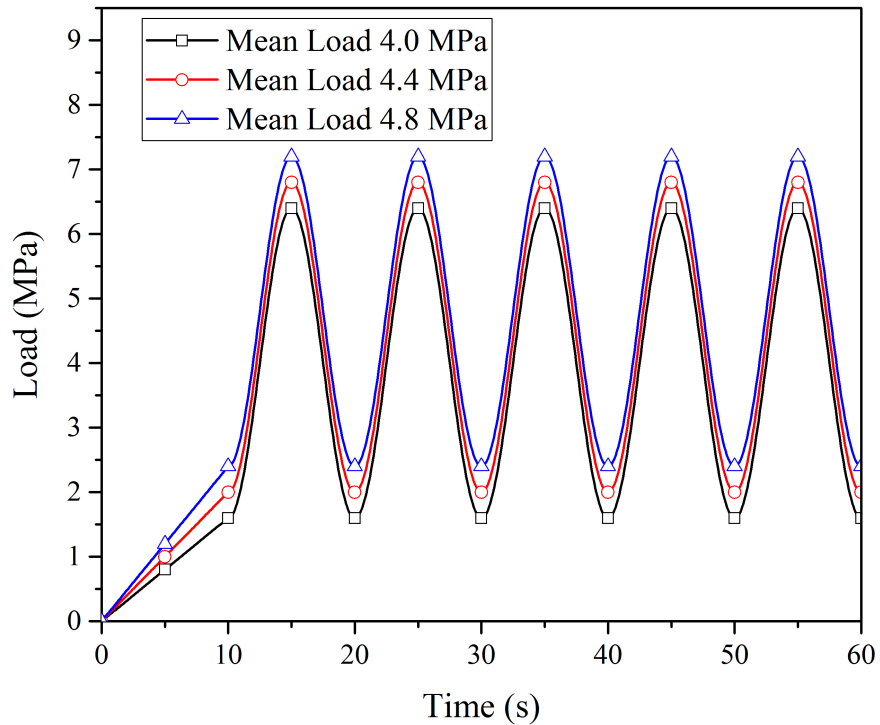


Figure 4-3 Cyclic loading profile in *ex-situ* mechanical fatigue testing.

Cyclic fatigue tests were conducted with different combinations of mean load, temperature and relative humidity (RH) and the lifetime (number of cycles to failure) was recorded for each combination. The results are shown in Figure 4-4 and Figure 4-5. Notice in Figure 4-4 at 25 °C and in Figure 4-5 at 25 °C and 50% RH, the membrane survived the number of cycles shown in the graph without breaking and the experiment was stopped due to time considerations. These numbers do not imply that the lifetime is the number of cycles shown in the graph.

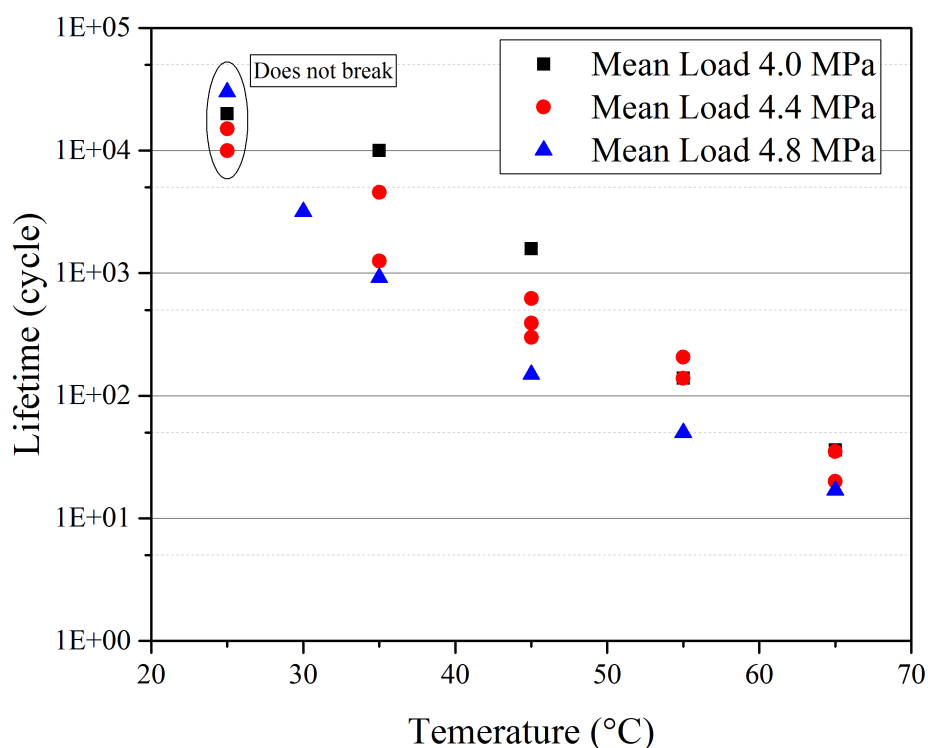


Figure 4-4 Effect of temperature and mean load on the lifetime of Nafion® 211 membranes at RH 50%.

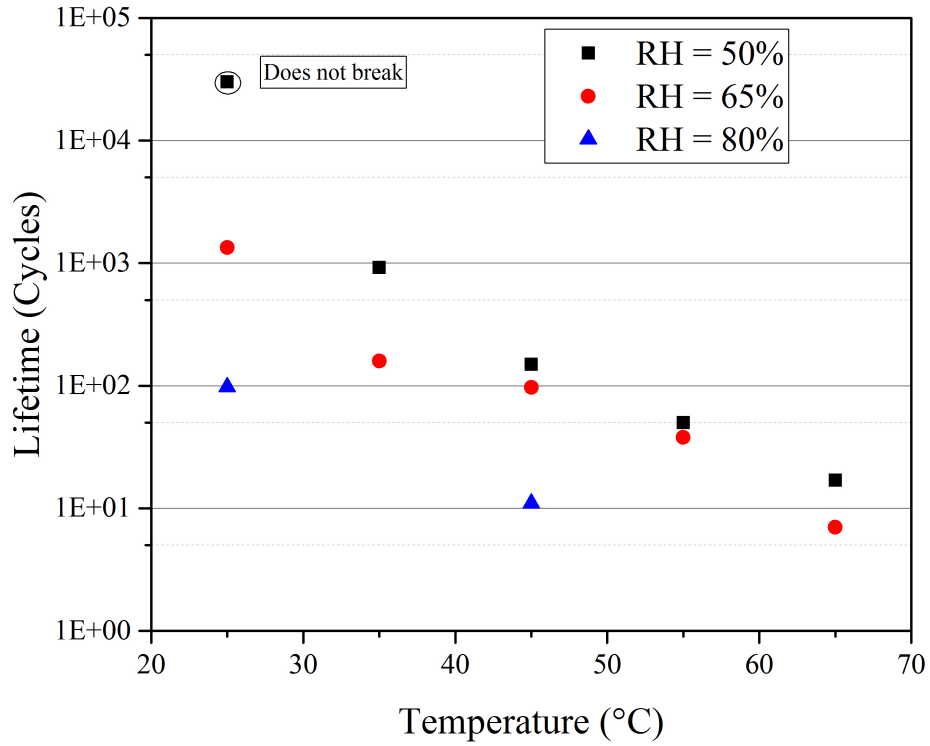


Figure 4-5 Effect of temperature and RH on the lifetime of Nafion[®] 211 at mean load of 4.8 MPa.

4.3 Finite Element Model

A two-dimensional plane stress finite element model is created using the commercial finite element package ABAQUS [102] as is illustrated in Figure 4-6. At the bottom edge, fixed boundary conditions are applied to simulate the grip. At the top edge, roller boundary conditions which constrain the x-displacement are applied to simulate the extension via a rigid clamp. A uniform pressure load is applied at the top of the edge with the load profile illustrated in Figure 4-3 for each mean load level. The

Nafion[®] 211 membrane is modeled using the viscoelastic-plastic material property parameters determined in Khattri et al. [76], and Poisson's ratio of 0.4 [118].

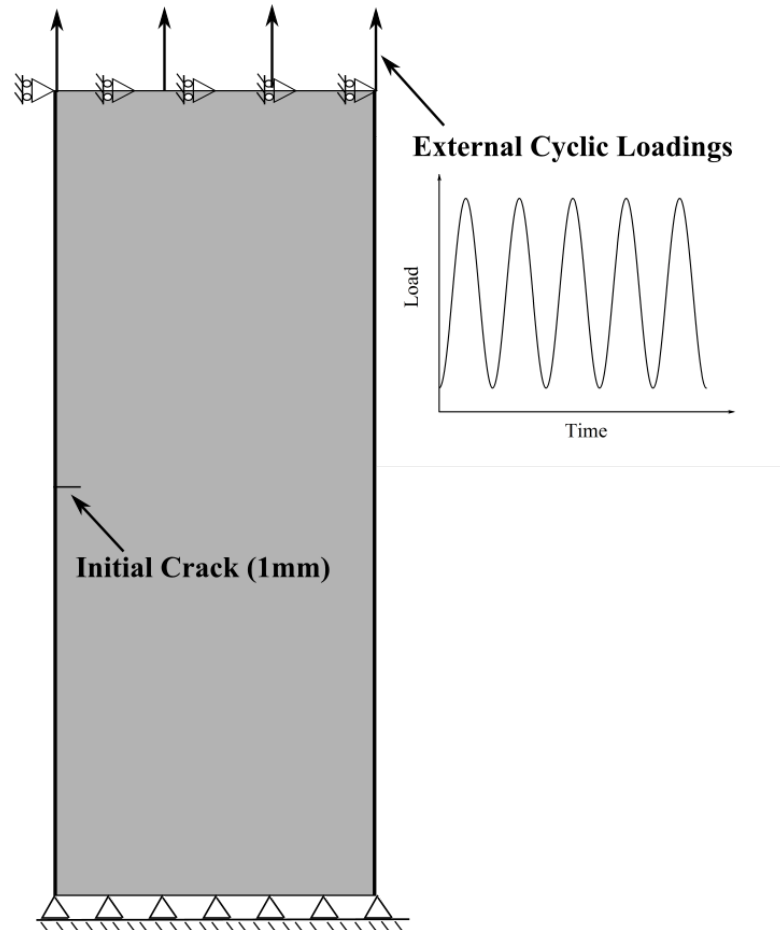


Figure 4-6 Two-dimensional finite element model of the Nafion[®] 211 membrane specimen.

4.4 Result and Discussion

To establish the critical value of plastically dissipated energy, three experimental values of the number of cycles to failure under different conditions are chosen. The critical value of plastically dissipated energy is determined from one test

condition, and is used in the other two for verification. From the experimental results shown in Figure 4-4, at 45 °C and RH 50%, the lifetime at mean load of 4.8 MPa is 149 cycles. Assuming that the crack propagates through the membrane when the specimen fails, the crack growth is 19 mm and the average crack growth rate da/dN is 0.127 mm/cycle. The accumulation rate of plastically dissipated energy, dW_p/dN , determined from simulation is 6.35E-4 N·mm/cycle. Using Equation (2.2), the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$, is calculated as 5.0E-3 N·mm/mm. Here da/dN and dW_p/dN are assumed to be constant to simplify the calculation and to verify the applicability of the method.

The estimated crack growth rate for the other two conditions are calculated using Equation (2.1). Assuming that the crack propagates through the membrane specimen when the specimen fails (i.e., the crack grows by 19 mm), the number of cycles to failure can be estimated and is then compared with the actual number from experiments. The results are listed in Table 4-1.

Table 4-1 Estimated cycles to failure at temperature 45 °C, RH 50% and mean load 4.0 MPa, and at temperature 25 °C, RH 50% and mean load 4.8 MPa

	Mean Load 4.0 MPa Temperature 45 °C RH 50%	Mean Load 4.8 MPa Temperature 25 °C RH 50%
dW_p/dN (N·mm / cycle)	2.9E-4	2.1E-4
da/dN (Estimated) (mm / cycle)	0.058	0.42
Number of cycles to failure (Estimated)	330	450
Number of cycles to failure (Experiment)	1580	>30,000

For mean load of 4.0 MPa, 45 °C and 50% RH, the number of cycles to failure from the experiment is 1,580, while the estimated number is 330. What's more, for mean load of 4.8 MPa, 25 °C and 50% RH, the number of cycles to failure from the experiment is more than 30,000, while the estimated number is only 450.

Therefore, the relationship for the number of cycles to failure is not captured using the plastically dissipated energy criterion. There are several possible reasons for the mismatch between the experiments and the simulations.

First, it was found from experiment that under cyclic fatigue loading, the membrane deformed in the out-of-plane direction (wrinkling). Therefore, the two-dimensional plane stress model was not an accurate way to model the experiments. To better model the experiment, a three-dimensional model with shell elements or three-dimensional continuum elements may be needed. Alternately, it may be possible to develop an experimental setup to prevent the out-of-plane deformation of the membrane under cyclic fatigue loading.

Second, the actual failure mechanism of the membrane in the *ex-situ* experiment is not clear. The experiment was conducted inside an environmental chamber, so the failure process was not monitored visually. The membrane may have failed due to gradual fatigue crack growth or sudden fracture failure. In addition, fatigue cracks may have grown to different lengths prior to overall failure under different conditions. An effective way to monitor the membrane inside the environmental chamber will provide more insights into the actual failure mechanism.

4.5 Synopsis

In this chapter, attempts made to determine the critical value of plastically dissipated energy for unreinforced PFSA are discussed. *Ex-situ* mechanical fatigue testing was conducted on pre-cracked rectangular Nafion[®] 211 membranes at different combinations of temperature, relative humidity (RH) and mean loads, and the numbers of cycles to failure were recorded for each case. Then a two-dimensional plane stress model was created to simulate the fatigue tests and to determine the critical value of plastically dissipated energy. However, the simulation was not able to capture the numbers of cycles to failure data obtained from experiments. It was observed that the membrane deformed in an out-of-plane direction during cyclic loadings, so the two-dimensional plane stress model may not be a proper model to simulate the experiment. What's more, the actual failure mechanism of the membrane under the cyclic loading was not clear as the membrane was not monitored inside the environmental chamber. Therefore, more experimental and simulation efforts are still needed to establish the critical value of plastically dissipated energy for PFSA membranes.

Chapter 5

CONCLUDING REMARKS AND FUTURE WORK

5.1 Summary of Dissertation

Fatigue failure, the phenomenon that under cyclic loading materials or structures fail at load levels that are well below the load levels required to fail them under static loading, has been estimated to contribute to 60% to 80% of the failure of mechanical components. Characterization and modeling of fatigue crack growth is an important step in understanding fatigue failure and predicting fatigue life.

Experimental characterization is commonly used, but is generally expensive, time-consuming and not always reliable. Numerical modeling using finite element analysis is a useful way to reduce the time and cost associated with experimental characterization, and the motivation of this dissertation stems from the need for an effective method to numerically model fatigue crack growth under cyclic loadings.

The plastically dissipated energy is directly linked to the net accumulation of plastic deformation, which is associated with material degradation during fatigue crack growth under cyclic loadings, and therefore can serve a criterion to assess fatigue crack growth. The plastically dissipated energy has been previously applied to investigate fatigue crack growth behavior in metals. This dissertation addresses the extension and application of the plastically dissipated energy criterion to numerical modeling of fatigue crack growth in a variety of polymers and structures.

The following is the summary of the tasks undertaken and conclusions drawn in this work.

Paris-regime crack growth in polymers: Paris-Law behavior is an empirical description of fatigue crack growth in metals and polymers. The plastically dissipated energy has been previously applied to evaluate Paris-regime crack growth rate in metals. In this work, the plastically dissipated energy criterion was adopted to study Paris-regime crack growth in polymers. The crack growth rate, da/dN , was expressed as the accumulation rate of plastically dissipated energy in the dissipation domain at the crack tip, dW_p/dN , divided by the critical value of plastically dissipated energy required per incremental increase in crack length, $(dW_p/da)_{cr}$. dW_p/dN at different ΔK levels were obtained by probing the accumulation of plastically dissipated per load cycle in a dissipation domain that fully captures the initial reverse plastic zone using a two-dimensional finite element model of a standard compact tension (CT) specimen under plane strain conditions. $(dW_p/da)_{cr}$ was assumed to be a material property and it must be determined from experiment. Currently, to the knowledge of the author, there is no experimental data available in literature on this value. Therefore, in this work, $(dW_p/da)_{cr}$ was determined by matching one simulation (ΔK , dW_p/dN) data point with one experimental (ΔK , da/dN) data. Paris-regime crack growth curves were constructed for PC and Nylon 66, whose Paris-regime crack growth behavior is independent of testing frequency, and for PS, PVC and PMMA, whose crack growth behavior is dependent on testing frequency. The numerically predicted Paris-regime crack growth curves were in good agreement with experimentally obtained Paris-regime crack growth curves for both the frequency-independent and frequency-dependent polymers studied.

***In-situ* crack growth in polymer electrolyte membrane:** Understanding the crack growth in polymer electrolyte membrane during cyclical hygrothermal loadings

is essential to improving the mechanical durability of the membrane. The plastically dissipated energy criterion was further extended to study *in-situ* fatigue crack growth in polymer electrolyte fuel cell membranes under relative humidity (RH) cycles. The accumulation of plastically dissipated energy in the dissipation domain at the crack tip, ΔW^p , was compared with the critical value of the plastically dissipated energy, W_{cr}^p . Once the critical value of plastically dissipated energy was reached, the crack was made to propagate via a node-release scheme. The critical value of plastically dissipated energy, W_{cr}^p , is a material property and can only be determined from experiments. In the current investigation, this was not known and therefore it was given an assumed values to obtain reasonable overall simulation time and to test the viability of the proposed methodology in studying fatigue crack growth in polymer electrolyte fuel cell membranes. The actual critical value of plastically dissipated energy can be implemented into the model once it is established from experiments. Crack propagation in PEM fuel cell membranes under RH cycling was simulated in two-dimensional representative PEM fuel cell models created in the commercial finite element package ABAQUS. It is well-established experimentally that during RH cycling, the crack tip will blunt and that ePTFE reinforced PSFA membranes offer better durability than unreinforced PFSA membranes. From experimental and in field observations, through-thickness membrane cracks are generally found under the channel regions but not under the land regions. Also within certain limits, increasing clamping on the fuel cell improves the mechanical durability of the membrane. Finally, experimental data shows that the number of RH cycles to failure depends on the hold time at the saturated and dry conditions, with the longer hold time at saturated and dry conditions leading to a smaller number of cycles to failure. These conditions

were all investigated within the context of the finite element model and the proposed plastically dissipated energy criterion captured all of these observations qualitatively.

Establishing the critical value of the plastically dissipated energy for

PFSA membrane: The critical value of plastically dissipated energy is a material property, and therefore must be determined from experiment. Attempts were made to determine the critical value of plastically dissipated energy for PFSA membrane by first conducting *ex-situ* fatigue testing on Nafion[®] 211 membranes and then conducting finite element analysis to match the experimental data. Nafion[®] 211 specimens (20 mm by 50 mm with a 1mm pre-existing crack) were tested using an MTS[®] 858 Mini Bionix[®] II material testing system with an ESPEC[®] environmental chamber under different combinations of temperatures, relative humidity (RH) and mean loads. The numbers of cycles to failure for each case were recorded. Then a two-dimensional plane stress model was created using the commercial finite element package ABAQUS to determine the critical value of plastically dissipated energy. Unfortunately, the simulation failed to capture the numbers of cycles to failure data obtained from experiments. The membrane was found to deform in the out-of-plane direction (wrinkling) during *ex-situ* cyclic loading, so three-dimensional models are needed to accurately simulate the experiment. Alternately, extra experimental designs are needed to prevent the out-of-plane deformation of the membrane. In addition, the actual failure mechanism of the membrane was not clear as the *ex-situ* experiment was conducted in an environmental chamber and the failure process was not monitored visually. An experimental setup to monitor the membrane needs to be developed to provide more insight into the actual failure mechanism. Therefore, more experimental and simulation efforts are required to establish the critical value of plastically

dissipated energy for PFSA membrane. Once the critical value of plastically dissipated energy is determined, it can then be implemented into the numerical scheme presented in Chapter 3 to provide more quantitatively meaningful results on the *in-situ* crack growth behavior in polymer electrolyte membranes.

In summary, this dissertation extended the application of plastically dissipated energy to study fatigue crack propagation in a variety of polymers, loadings and structures. The author believes that the proposed method of plastically dissipated energy can be used to estimate fatigue crack growth for a range of ductile materials based on limited fatigue testing and can therefore potentially reduce the cost and time of introducing new materials in engineering structures.

5.2 Future Work

Improvements and extension of this work can be realized by:

First, a node-release scheme is implemented to develop the plastic wake and model crack growth. The major limitation of the node-release scheme is that the crack path has to be predefined. Evaluation of the crack trajectory can be of equal importance to evaluation of the crack growth rate in modeling fatigue life. The plastically dissipated energy criterion can possibly be combined with other numerical techniques such as generalized finite element methods or extended finite element methods to lift the limitation on predefined crack path and to enable predicting crack trajectories as well as the crack growth rates.

Second, the polymer electrolyte membrane generally undergoes thousands of relative humidity (RH) cycles before failure. Simulating this large number of RH cycles is computationally expensive and time-consuming. To reduce the

computational time, advanced techniques such as the cycle jump technique can be implemented into the numerical scheme to accelerate the simulation.

Finally, in simulating crack growth in ePTFE reinforced PFSA membranes, after the crack reaches the interface between ePTFE reinforcement and uPFSA membranes, the crack may continue to grow through thickness or continue to grow along the interface. The possibility of extending plastically dissipated energy criterion to study interface crack growth can be explored.

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