

Micromechanically informed reaction-induced damage and fracture in polymers due to oxidation

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Abstract

High temperature oxidation in polymers is a complex phenomenon, driven by the coupled diffusion-reaction process, causing changes in the amorphous network structure and resulting in property degradation. Prolonged oxidation in polymers results in the formation of a coarse, oxide layer on the outer surface and induces spontaneous cracking inside the material. In this paper, we present a chemical reaction-driven evolving network theory coupled with phase-field fracture to describe the effect of oxidation in polymers across different length scales. The theory considers the coupling between oxygen diffusion, chemical reactions, large deformation of polymers, and phase-field fracture in a thermodynamically consistent way. Guided by the statistical mechanics, the network theory has been introduced to model the reaction induced chain scissions and crosslinking events causing significant changes in the three-dimensional network structure. Further, these microscale events have been considered as the reason behind macroscopic mechanical property degradation, namely oxidative embrittlement. Finally the network theory is coupled with a phase-field fracture model to capture the macroscale damage and fracture in the polymer under stress-coupled oxidation conditions. We derive the specific constitutive forms for all the physical-chemical processes based on the thermodynamic inequality conditions, and numerically implement the theory in finite elements by writing ABAQUS user-defined element (UEL) subroutine. To present the model's capability, numerical examples with standard fracture geometries have been studied.

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The simulation results have demonstrated the model’s capability of predicting the effect of oxidative aging on the polymer’s response.

Keywords: thermodynamically consistent, phase-field fracture, statistical mechanics, transient network theory, large deformation, oxidative aging, chemo-mechanically coupled, chemical reactions, amorphous polymers, oxygen diffusion

1. Introduction

High temperature oxidative aging in polymers and polymer matrix composites (PMCs) involves a multi-scale damage and fracture process that starts at a molecular level with multiple chain reactions, leading to the microscale chain-scission and oxidative crosslinking. These microscale events eventually degrade the material properties at the macroscale and adversely effect the mechanical response of the polymers [45, 65, 68, 69, 91]. Oxidation in polymers at high temperature is characterized as a coupled diffusion-reaction phenomenon driven by the diffusion of atmospheric oxygen. The damage induced by oxidation significantly alters the constitutive response of the polymer and notably reduces the life-time expectancy. Polymeric materials are greatly desirable in many applications for excellent exhibition of competing properties, (such as light weight, toughness, viscous dissipation, etc.). However, the current literature is still limited in terms of the accurate response predictions of these materials at high temperature oxidative environment, such as, in the components of supersonic jets, pipelines and chemical storage etc. [30]. The experimental studies regarding the high temperature oxidation in polymers can be categorized into two groups:- i) microscale characterization- mainly focuses on quantifying the bond formation/scissions and the oxidative products through Fourier or Raman spectroscopy [21, 72, 73, 85], ii) macroscale characterization- those reported property changes in polymers and PMCs through combined macro and micrographic observations. Studies were done to measure the oxide layer thickness and to estimate an increase in the modulus, decrease in the glass transition temperature, shrinkage strain development and decrease in the failure strain, via indentation test, dynamic mechanical analysis (DMA), tensile and bending tests combined with SEM images

[30, 33, 37, 39, 40, 47, 48, 64, 68, 69, 91]. Also, identification of the other inevitable effects of thermal oxidation in case of PMCs as the matrix microcracking and debonding at the fiber-matrix interfaces, are reported in [16, 45, 47, 64, 76]. These experimental studies in micro and macro scales reveal that, during oxidation, properties of the polymers experience significant alteration, caused due to a competing chain scission and crosslinking events at the microscale [19, 21, 26, 27]. These microscale events, as driven by the closed loop chain reaction, interact with the macroscale deformation and stress resulting in damage and fracture of the polymer specimens.

Modeling of thermo-oxidative aging is an integral part of the study. While experiments are inevitable to characterize the property changes in the course of oxidation, it may sometimes render inadequate to gather all the information regarding material behavior at all the possible scenarios. In reality, the effect of high temperature oxidation in polymer is a slow process requiring days or months to demonstrate measurable changes in polymer response. However, the experiments are commonly being conducted at accelerated aging conditions [21]. Therefore, modeling the oxidation in polymers has always been a strong focus of the polymer literature. The most popular model is the mechanistic model, which was developed by a thorough investigation of the oxidation reaction kinetics [11]. The property degradation can be linked to the reaction products, which can be calculated based on the mass balance of each individual reactants and products [39, 40]. While using the mass balance, it is important to note that each reactant takes part in the multiple closed loop chain reactions, as described in [9–11, 25–31, 73, 89]. An extension of this model can also be found in the literature, known as the three zone oxidation model, that emphasized in the heterogeneity of oxygen diffusion leading to an oxide zone formation followed by an active reaction zone and then an unoxidized core [70, 81, 82]. This heterogeneity in the degree of oxidation results in non-uniform mechanical properties and inhomogeneous stress/strain distribution within an oxidized polymer [46, 47, 81]. In the similar trend, a diffusion-limited oxidation (DLO) model is also introduced to predict oxidation within a thick polymer sample [20, 21]. The DLO predictions showed that when the rate of reaction is greater than that of oxygen diffu-

sion, the reaction gets contained within the surface instead of spreading toward the sample core [20, 21, 71]. Recently, a micro-mechanical model based on the competition between chain-scission and crosslinking events occurring at the polymer network during oxidation was reported to predict the changes in the constitutive behavior of polymers by [66]. On the other hand, a thermodynamically consistent continuum model to predict the constitutive response based on high-temperature oxidation behavior was found in the work of [46, 47]. However, these models do not consider the connection between the micro-scale polymer network evolution with the macroscopic fracture and property degradation in a stress-coupled situation, during oxidative aging.

Thermo-oxidative aging process leads to a gradual change in the material's configuration at the microscale, before any visible macro cracks or other fracture zones appear. The main contributing factor to this microscale alteration is the evolution of the original polymer network with scissored and newly- formed crosslinked networks. Describing these changes at microscale through the statistical mechanics description of polymer chains, seems to be more fitting as this approach enables a more detailed connection with the statistics of the polymer chains, [34, 57, 80, 83, 86, 88, 90]. Assuming that the statistical distribution of the polymer network can be altered through the chain scission/crosslinking events, one can readily track the effect of oxidation via the evolution of a so-called chain distribution function. Further considering an affine deformation of the polymer network, one can establish a direct link between the micro and macro scale kinematics, as done in the entropic elasticity theories. In literature, a number of such statistical models are found, for example, the eight chain model ([8]), the fully network model ([90]), the transient network theory ([88]), a bond deformation energy based model ([59]), to name a few.

In order to fully understand the behavior of the polymers undergoing oxidation and their lifetime expectancy during application, a suitable model to capture the damage and fracture across different length scales is indispensable and still lacking in the literature. The macroscale damage and fracture in polymers undergoing oxidation is the result of a highly nonlinear, stress-coupled, diffusion-reaction process. As the heterogeneous diffusion-reaction

process coupled with mechanical deformation leads to an inhomogeneous damage propagation within the polymer, a phase-field fracture model seems to be better suited to predict this oxidative aging process at the macroscale. Phase-field fracture model has been successfully incorporated to solve various multi-physics problems in the literature [6, 12, 58, 60, 62, 67, 79]. The model is also beneficial to implement numerically within a variational setting of the proposed problem compared to a phenomenological discrete crack or cohesive zone model [14, 15, 42, 61, 63]. An excellent review on the phase-field modeling of brittle fracture can be found in [2]. In order to overcome the difficulties in classical Griffith-type theory of brittle fracture, phase-field fracture was originally derived from the variational methods based on energy minimization as suggested by [14, 17, 32, 42]. The key feature of the phase-field fracture lies in the approximation of a sharp crack topology in the solid by regularized diffusive crack zones governed by a scalar auxiliary variable ' d '. This variable can be considered as a phase-field order parameter which interpolates between the undamaged ($d = 0$) and a completely broken state of the material ($d = 1$). Further, introducing a crack surface density function, the dissipative fracture energy can be quantified in terms of the bulk (volumetric) quantity and be combined with the stored energy of the solids for minimization [13, 14, 61, 63].

In this paper, we develop an oxidation reaction-informed evolving network theory coupled with phase-field fracture to connect the microscale network evolution with macroscopic fracture occurring in polymers during oxidative aging. We use the dynamic or transient network theory based on the statistical mechanics framework of the polymer chains, (as used in [74, 80, 83, 86, 88]), to model the microscale network evolution yielded by the chemical reactions. According to this theory, we consider the evolution of the amorphous network in the polymer due to oxidation. The degree of crystallinity in a semicrystalline polymer also gets affected by the influence of high temperature but will not be considered in the present micromechanics. The configuration of a polymer network changes as chain scission and new crosslinked bonds are formed. To incorporate these microscale events, the proposed model considers the statistical distribution of the polymer chain configuration, assuming the end-to-end vector of a single chain as a primary kinematical quantity. We assume that this

distribution can evolve both as a function of mechanical deformation and oxidation reactions. The evolution of the chain statistics further affects the stored energy of the polymer system. We link this microscale chain distribution to the continuum kinematics description through the definition of a chain distribution tensor, as introduced in [88]. Further, the stored energy of the network is written in terms of this distribution tensor [74, 80, 88]. To connect this microscale mechanics with the macroscale damage and fracture under a stress-coupled oxidative situation, we use the phase-field fracture to model the macroscopic damage initiation, crack propagation and ultimate fracture. The framework is developed in a thermodynamically consistent way to model the coupling between various physical-chemical processes and to derive the specific constitutive forms for each of them, that prevails the oxidative aging in polymers.

The paper is organized as follows- firstly, we explain the chemistry of oxidation reactions in polymers followed by the statistical fundamental of the polymer chain network used in the standard network theory and how it would be modified in the present setting to incorporate the reaction-driven evolution. Considering the reaction modified polymer network, subsequently, we develop a continuum-level chemo-mechanically coupled theory incorporating phase field fracture to model the macroscale oxidative damage. The specific constitutive forms are then derived for each individual process. We implement the proposed theory in a finite element setting by writing a user element subroutine (UEL) in ABAQUS [1] and present several numerical simulations to demonstrate the capability of the model. At the end, the concluding remarks are presented.

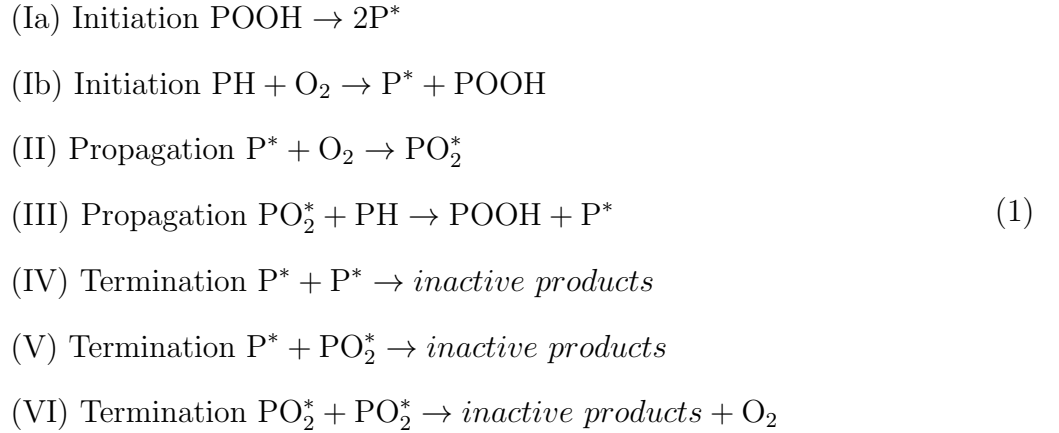
2. A reaction-dependent network theory coupled with phase-field fracture to model oxidative aging in polymers

As mentioned earlier, during oxidation, polymer undergoes a series of chain reactions that leads to random chain scission and oxidative cross-linking at the microscale (as shown in Fig 1b). These microscale events further interact with the polymer’s general state of stress and result into macroscopic property degradation and fracture. In the present section

we describe a micromechanically informed, chemo-mechanically coupled theory to connect the microscale modifications in the polymer network due to oxidation with the macroscopic fracture under mechanical loading.

2.1. Chemistry of oxidation:- the reaction kinetics

To understand the multiple chain reactions involved in the case of a polymer undergoing oxidation, we briefly summarize the underlying reaction kinetics. The mechanistic reaction schemes proposed to describe the thermal oxidation in polymers had a consensus in the literature except for some minor variation at the initiation stage [9–11, 25–31, 73, 89]. According to this standard mechanistic scheme, during oxidation, the polymer undergoes six sets of closed-loop chain reactions involving three major steps identified as initiation, propagation, and termination, respectively, as explained below:



where PH represents the polymer substrate; P^* is the alkyl radicals; POOH is the hydroperoxide, PO_2^* is the peroxy radical and O_2 represents oxygen. These set of reactions were originally proposed by [31] and then followed in the polymer chemistry literature, [9, 28, 29, 31], to describe the chemistry of the oxidation process. Incorporating the reaction kinetics in a coupled diffusion-reaction-deformation framework a theory has been presented in our recent work [52], to model oxidation coupled large deformation constitutive behavior in polymers.

2.1.1. Extent of reaction

To connect the reaction kinetics occurring at the molecular level with the micro-scale events such as chain scissions and crosslinking, we introduce a scalar quantity, as *extent of reaction*, to describe each individual reaction [52]. These extent of reactions are a measure of aggregates for each reaction happening during oxidation. We define the extent of reaction for each reaction (n) at every continuum point $\mathbf{X}$ in a local dimensionless form as,

$$0 \leq \xi_n(\mathbf{X}, t) \leq 1 \quad (2)$$

where ' n ' is the number of reaction and varies between 1 to 6 depending on the oxidation kinetics for a specific polymer. Since polymer oxidation is a multi-component system involving multiple reactions (as described earlier), the chemical concentration for any component β would change depending on the extent of all the reactions in which it is participating, as,

$$r^\beta = \sum_n \left[\mathcal{R}_{n\beta} \dot{\xi}_n \right] \quad (3)$$

where r^β is the rate of production or consumption of chemical species β (measured in moles per volume) and $\mathcal{R}_{n\beta}$ is the stoichiometric coefficient in reaction n .

2.2. A reaction-dependent network theory based on the statistical mechanics of polymer chains

At the outset, we consider most of the polymer chains are attached to each other in an amorphous network via cross-links, representing a 3D solid polymer at its virgin state. We also assume that, the actively crosslinked chains in the network essentially provides the structural integrity for the polymer. In addition, the network also contains some dangling chains representing the unstable hydroperoxides, which could act as the initiator for the oxidation reaction. Hence, the total number of chains in a polymer network (C_T) is the sum of the active and inactive chains. Following [50], under the assumption that individual chains do not diffuse within the polymer, the total concentration follows the standard conservation equation as,

$$\dot{C}_T + C_T \operatorname{tr}(\mathbf{L}) = 0 \quad (4)$$

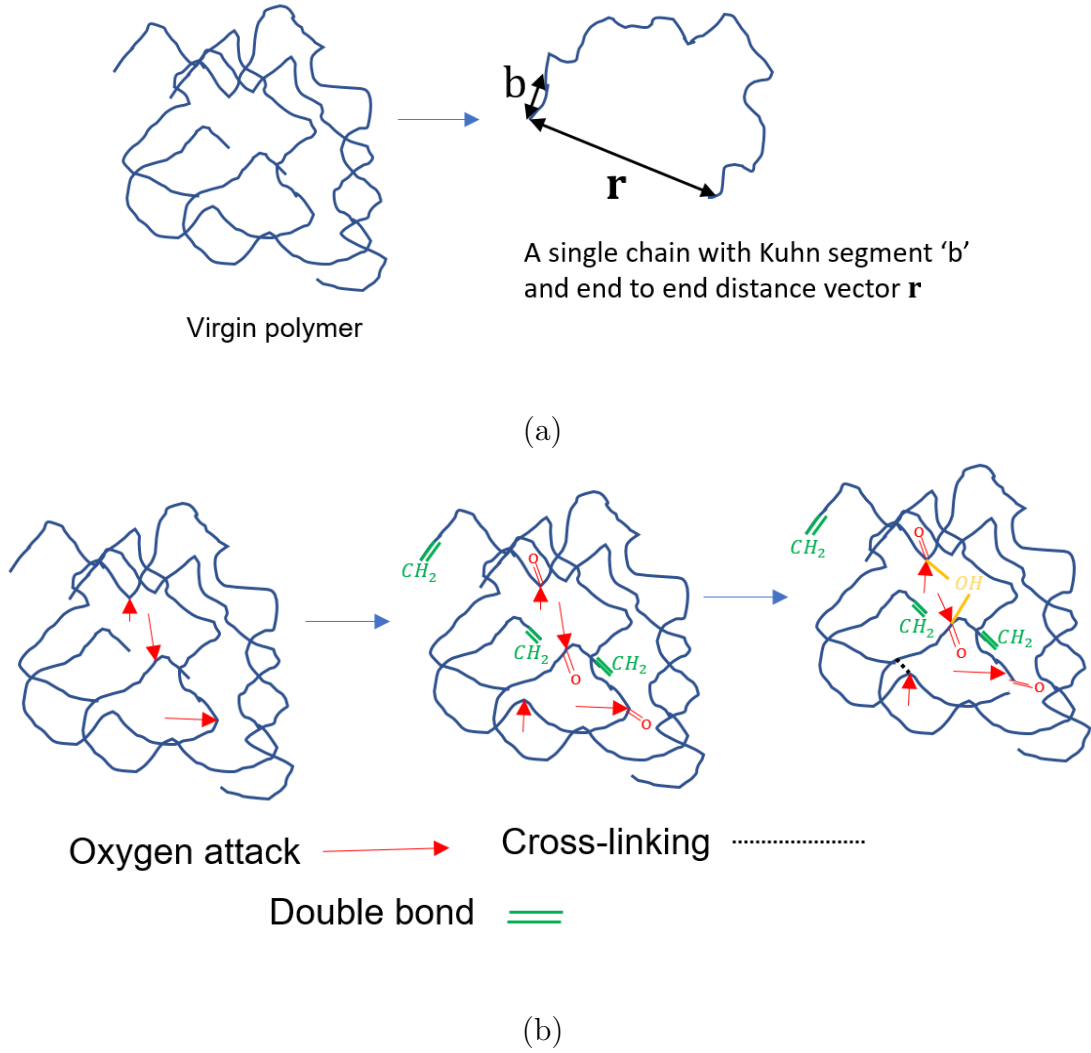


Figure 1: (a) Typical virgin polymer chains with Kuhn segment 'b' and end to end distance vector $\mathbf{r}$, (b) polymer undergoing oxidation developing new cross-links and broken chains.

with $\mathbf{L}$ representing the velocity gradient as $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$, where $\mathbf{F}$ is the deformation gradient. During oxidation, some polymer chains get broken (via reactions (I) and (III)). Since polymer radicals are highly reactive, these broken chains can get re-attached via the termination reactions (IV, V and VI). These new attachments or bonds are formed with a much lower energy compared to the original bonds in the virgin networks as reported in [66]. Thus, one can consider that, the final oxidative product has more cross-linked network of smaller chains compared to the virgin polymer with longer cross-linked network. It is important

to mention that, oxidation reaction gives rise to a different type of network in the oxide zone of the polymer, a "PO-OP" type network compared to the original P-P network. We attempt to describe the polymer oxidation phenomena as a collective response of the chain detachments and attachments at the microscale governed by the chain reactions. With the help of a chain distribution function based on the chain end-to-end vector $\mathbf{r}$, (motivated by the transient network theory as introduced in [80, 86–88]), we use a statistical framework to describe the physical state of an oxidized polymer network. Further, we incorporate the reaction kinetics to formulate an evolution equation for this chain distribution. Finally, introducing the second moment of this distribution, termed as '*chain distribution tensor*' the macroscopic free energy of the polymer can be derived. It is important to note that one of the key limitation of this theory while deriving the free energy is the assumption of Gaussian statistics of the polymer chains, which had been circumvented by [87], with the use of so-called mean field approximation. In the present study we also assume that this approximation is valid and the rate of attachment/detachment events due to oxidation reactions are independent of mechanical deformation.

2.2.1. Chain distribution function

To begin with, we consider the end-to-end vector ($\mathbf{r}$) of a single chain as a primary kinematical quantity to describe the polymer chain configuration. Let us consider that every single chain is comprised of N number of freely joined Kuhn segments of length b as demonstrated in Fig. 1a. As postulated in the classical random walk model, we assume that all the actively crosslinked chains are of equal length. Hence, the physical state of the polymer can be represented by the statistical distribution of the end-to-end vectors ($\phi(\mathbf{r})$) for the entire chain population. Let us consider that, the distribution function $\phi(\mathbf{r})$ can be expressed by a simple relationship between the probability density function $P(\mathbf{r})$ and active chain concentration $c(t)$ as,

$$\phi(\mathbf{r}, t) = c(t)P(\mathbf{r}, t) \quad (5)$$

where $c(t)$ has the unit of number of chains per unit of current volume. The active chain concentration is the integral of all the possible chain distributions, $\phi(\mathbf{r}, t)$ and can be written

as,

$$c(t) = \langle \phi \rangle \quad (6)$$

where the operator $\langle \blacksquare \rangle$ indicates the integral over all the possible chain configuration as,

$$\langle \blacksquare \rangle = \int_0^{2\pi} \int_0^\pi \left(\int_0^\infty \blacksquare r^2 dr \right) \sin\theta \, d\theta \, d\omega \quad (7)$$

where θ and ω are the direction of the end-to-end vector $\mathbf{r}$ in the spherical coordinates. Further assuming that, at a length-scale much larger than the individual chains, the network is random and isotropic, the stress-free chain distribution can be expressed as a normal distribution $P_0(\mathbf{r})$ with a zero mean and a standard deviation $\sqrt{N/3}b$ in each of the three spatial directions. We use the expression from [83] for $P_0(\mathbf{r})$ as,

$$P_0(\mathbf{r}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3|\mathbf{r}|^2}{2} \right) \quad (8)$$

which leads to the chain distribution at stress-free configuration as,

$$\phi_0(\mathbf{r}, t) = c(t_0)P_0(\mathbf{r}) \quad (9)$$

where $c(t_0)$ is the active chain concentration at the stress-free configuration at time $t = t_0$.

2.3. Evolution of chain distribution due to the combined effect of oxidation and mechanical deformation

The hypothesis is that in a network of polymer chains, the statistical distribution of $\mathbf{r}$ changes as a function of mechanical deformation and chemical reactions. As both the deformation and the oxidative reactions cause changes in the chain distribution $\phi(\mathbf{r}, t)$ and active chain concentrations $c(t)$ within an amorphous network, we can write,

$$\dot{\phi}(\mathbf{r}, t) = \dot{\phi}(\mathbf{r}, t)\Big|_{ox} + \dot{\phi}(\mathbf{r}, t)\Big|_{\mathbf{F}} \quad (10)$$

The first term represents the change in the distribution due to mechanical deformation and the second one considers the change due to chemical reactions holding the deformation constant. The subscripts *ox* and $\mathbf{F}$ denote oxidation and deformation gradient, respectively.

Assuming an affine deformation such that the end-to-end vectors of all chains evolve proportionally with respect to the macroscopic deformation gradient [88], we can write the 1st term of Eq. 10 as,

$$\dot{\phi}(\mathbf{r}, t) \Big|_{ox} = -\mathbf{L} : (\nabla \phi \otimes \mathbf{r}) \quad (11)$$

where $\mathbf{L}$ is the macroscopic velocity gradient. Following the definition of spatial time derivative and the use of transport theorem over the chain distribution space, the derivation of the final form of Eq. 11 is not new and can be found in literature [88]. In this work, we investigate the 2nd term in further details, which incorporates the change in the chain distribution arising from the oxidation reactions.

As we can see from Eq. 1, chain dissociation or scissions occur during reaction (Ia), (Ib) and (III) and chain reattachment happens in reaction (IV), (V) and (VI). We assume that, the chain scission is proportional to the current distribution function $\phi(\mathbf{r}, t)$ and depends on the scission reactions. We further assume that, chain attachment happens in a stress-free configuration and dependent on the termination reactions. Also, only a fraction of chains that has been scissioned before gets reattached in the termination process. Hence, one can write a kinetic form to accommodate the change in the chain distribution due to the reactions as,

$$\dot{\phi}(\mathbf{r}, t) \Big|_{\mathbf{F}} = f_a(\xi_n) c_d(t) P_0(\mathbf{r}) - f_d(\xi_m) \phi(\mathbf{r}, t), \text{ with } m = 1a, 1b, 3 \text{ and } n = 4, 5, 6 \quad (12)$$

where $c_d(t)$ equals the total number of detached or scissioned chains and f_a and f_d are the reaction dependent functions. Further m, n denotes the reaction number, and $P_0(\mathbf{r})$ is the probability of chain configuration in the stress-free state. The number of detached chains can be found as, $c_d(t) = C_T - c(t)$. In addition, we assume that, the reaction dependent functions can be expressed as follows:

$$\begin{aligned} f_d(\xi_m) &= k_d(\xi_{1a} + \xi_{1b} + \xi_3) \\ f_a(\xi_n) &= k_a(\xi_4 + \xi_5 + \xi_6) \end{aligned} \quad (13)$$

where k_d and k_a are rate-like reaction dependent coefficients, that denote the chain detachment and attachment rates, respectively. Substituting Eq. 13 into Eq. 12, we can get the evolution of the chain distribution due to the reaction as,

$$\dot{\phi}(\mathbf{r}, t)|_{\mathbf{F}} = k_a(\xi_4 + \xi_5 + \xi_6)(C_T - c(t))P_0(\mathbf{r}) - k_d(\xi_{1a} + \xi_{1b} + \xi_3)\phi(\mathbf{r}, t) \quad (14)$$

Substituting Eq. 11 and 14 into Eq. 10 yields the complete evolution equation for the chain distribution as,

$$\dot{\phi}(\mathbf{r}, t) = -\mathbf{L} : (\nabla\phi \otimes \mathbf{r}) + k_a(\xi_4 + \xi_5 + \xi_6)(C_T - c(t))P_0(\mathbf{r}) - k_d(\xi_{1a} + \xi_{1b} + \xi_3)\phi(\mathbf{r}, t) \quad (15)$$

2.3.1. Evolution of the concentration of active chains

Following Eq. 6, one can see that, the active chain concentration is the integral of all the possible chain distribution function, $\phi(\mathbf{r}, t)$. As the chain distribution evolves, the concentration of the active chains would also change with time. Using the fact, $\dot{c} = \langle \dot{\phi} \rangle$ and by integrating Eq. 15 over the chain space, we can write the evolution of the chain concentration as,

$$\dot{c} = k_a(\xi_4 + \xi_5 + \xi_6)(C_T - c(t)) - k_d(\xi_{1a} + \xi_{1b} + \xi_3)c(t)\langle P(\mathbf{r}) \rangle - c(t) \text{tr}(\mathbf{L}) \quad (16)$$

where $\langle P(\mathbf{r}) \rangle$ represents the integration of the chain distribution over all the configuration and value of $\langle P_0(\mathbf{r}) \rangle = 1$ is used in the 1st term. As per this expression, the active chain concentration would increase while the reaction kinetics are dominated by the termination reactions and would decrease when the kinetics are dominated by the scission reactions. Also, the term, $\text{tr}(\mathbf{L})$ vanishes for an incompressible polymer. As the active chain concentrations provide rigidity in the polymer network, any change in the active chain concentration would directly influence the mechanical properties and stored energy of the polymer.

2.3.2. Active chain ratio and the dissociated chain ratio

The chain scission and crosslinking events due to the oxidation reactions influence the mechanical properties of the polymer network. In addition, the evolution of the active chain concentrations affect the network elasticity and the stress distribution in a polymer sample.

We define a non-dimensional parameter as a ratio between the current chain concentration $c(t)$ to the total chain concentration C_{T0} at the virgin state expressed as,

$$c_{rc} = \frac{c(t)}{C_{T0}} \text{ with } c_{rc} \leq 1 \quad (17)$$

This nondimensional quantity termed as "active chain ratio", attains a value of 1 for a fully crosslinked network. A value of $c_{rc} = 0$ represents a network without any crosslink (dilute chains). In an oxidative aging situation $c_{rc}|_{t=0} = c_{r0}$ represents the initial crosslinking density of the network, before any oxidation happened. Further, we also define another ratio termed as, dissociated chain ratio c_{rd} , which measures the concentrations of chains per mole that has been dissociated from the network ($c_d(t)$), normalized with respect to C_{T0} as,

$$c_{rd} = \frac{c_d(t)}{C_{T0}} \text{ with } c_{rd} \leq 1 \quad (18)$$

where $c_{rd} = 1$ represents a network completely dissociated and $c_{rd} = 0$ represents a fully crosslinked network.

2.3.3. Macroscopic property degradation due to oxidative embrittlement

The continuous occurrence of chain detachment/attachment events during oxidation alters the mechanical properties of the polymer network such as the shear modulus (G_{shear}), the limiting chain stretchability (λ_L) and the Griffith like fracture energy (G_c) etc. We assume that the mechanical stiffness or the shear modulus of the network is directly proportional to the active crosslinking density. Hence the shear modulus is expressed as a function of c_{rc} , as $G_{shear} \approx \Upsilon(c_{rc})$. In addition, due to chain scissions the molecular weight of the chains reduces and the ductility of the smaller chains drops significantly as a function of oxidative reactions [39, 40]. To quantify the drop in ductility we use the limiting stretchability of the network and express that as a function of scissioned chain concentration (c_{rd}). Similarly the fracture energy of the network also reduces as the average molecular weight of the network continues to drop [39, 40]. Hence, we assume the functional relations for λ_L and G_c , as,

$$\Gamma = \Xi_i(c_{rd}) \text{ , where } \Gamma \supset [\lambda_L, G_c] \quad (19)$$

The actual forms for the function Υ and Ξ_i ; $i = 1, 2$; will be discussed later in the specific constitutive forms. It is important to note that during the set of chain reactions prevailing oxidation, the degraded network essentially formed with smaller chains but more number of crosslinks [40]. Hence, there are studies where molecular weight of the new network has been used to characterize the increasing brittleness [39, 40]. In the present work, we have used the concentrations of the associated and dissociated chains which can directly be quantified with the reaction rates to correlate with the mechanical property changes.

2.4. The chain distribution tensor and the free energy of the oxidation reacted network

In order to connect the chain distribution function $\phi(\mathbf{r}, t)$ with the macroscopic description of the state of the polymer chain network at any stage of the deformation process, the chain distribution tensor ($\boldsymbol{\mu}$) is introduced as the second moment of the distribution, following [87, 88]. As mentioned earlier, assuming a Gaussian distribution for $P_0(r)$ at the stress-free configuration, $\boldsymbol{\mu}_0$ can be written as,

$$\boldsymbol{\mu}_0 = \langle P_0 \tilde{\mathbf{r}} \otimes \tilde{\mathbf{r}} \rangle \quad (20)$$

Evaluating the above expression using Eq. 7, results into identity tensor, $\mathbf{I}$. Other than the stress-free configuration, $\boldsymbol{\mu}$ is written as, $\boldsymbol{\mu} = \langle P \tilde{\mathbf{r}} \otimes \tilde{\mathbf{r}} \rangle$. Further assuming the distribution $P(\mathbf{r})$ still remains as Gaussian as the oxidation progresses, with different distribution parameters, $\boldsymbol{\mu}$ can be written as a symmetric (3×3) tensor. As it is well known, the symmetric tensor $\boldsymbol{\mu}$ can be better represented by three of its eigen values μ_i , $i = 1, 2, 3$; associated with its principal planes. The eigen values are related to the square of the standard deviation of the current end-to-end distance $\bar{r}_i^2$ as, $\mu_i = 3\bar{r}_i^2/Nb^2$; where $Nb^2/3$ is the mean-square end-to-end distance of the chains at stress-free configuration. More specifically, $\boldsymbol{\mu}$ can be directly connected to the average chain stretch as,

$$\bar{\lambda} = \frac{\bar{r}}{\bar{r}_0} = \sqrt{\frac{tr\boldsymbol{\mu}}{3}} \quad (21)$$

where, $\bar{r}_0$ is the root-mean-square (average) distance of the chain end-to-end vector at the stress-free configuration and $\bar{r}$ is the current root-mean-square value of the chain end-to-end

distance. By the very definition, the average chain stretch can be related to macroscopic right Cauchy-green strain tensor as follows,

$$\bar{\lambda} = \frac{1}{\sqrt{3}} \sqrt{\text{tr}(\mathbf{C})} \quad (22)$$

In elastomeric materials, the stored energy arises mainly due to entropic contribution. Hence the free energy of the material can be expressed as a function of $\bar{\lambda}$ based on the statistical theory of entropic elasticity as,

$$\psi_{\text{R}} = \bar{\psi}_{\text{R}} \left(G_{\text{shear}}, \frac{\bar{\lambda}}{\lambda_L} \right) \quad (23)$$

The specific form of the function ψ_{R} can be chosen as reported in [7, 43, 53] to incorporate the limiting chain extensibility of the network.

To obtain the evolution equation for $\boldsymbol{\mu}$, one needs to integrate the evolution equation for ϕ (Eq. 15) over the entire chain space. Finally it turns out as,

$$\dot{\boldsymbol{\mu}} = k_a(\xi_4 + \xi_5 + \xi_6) \left(\frac{C_T - c(t)}{c(t)} \right) \boldsymbol{\mu}_0 - (\langle k_d P \tilde{\mathbf{r}} \otimes \tilde{\mathbf{r}} \rangle) (\xi_{1a} + \xi_{1b} + \xi_3) - \frac{\dot{c}(t)}{c(t)} \boldsymbol{\mu} + \mathbf{D} \boldsymbol{\mu} + \boldsymbol{\mu} \mathbf{D} \quad (24)$$

where $\mathbf{D} = 1/2(\mathbf{L} + \mathbf{L}^T)$ is the symmetric part of the velocity gradient. The derivation of Eqn. 24 has been presented in earlier literature [87, 88], and hence avoided here. The term $(\langle k_d P \tilde{\mathbf{r}} \otimes \tilde{\mathbf{r}} \rangle)$ can be simplified by assuming that the dissociation rate k_d is independent of $\mathbf{r}$ and hence constant. Hence, we get, $(\langle k_d P \tilde{\mathbf{r}} \otimes \tilde{\mathbf{r}} \rangle) = k_d \boldsymbol{\mu}$. Replacing it in Eq. 24, we can re-write,

$$\dot{\boldsymbol{\mu}} = k_a(\xi_4 + \xi_5 + \xi_6) \left(\frac{C_T - c(t)}{c(t)} \right) \boldsymbol{\mu}_0 - k_d(\xi_{1a} + \xi_{1b} + \xi_3) \boldsymbol{\mu} - \frac{\dot{c}(t)}{c(t)} \boldsymbol{\mu} + \mathbf{D} \boldsymbol{\mu} + \boldsymbol{\mu} \mathbf{D} \quad (25)$$

The two specific cases for $\boldsymbol{\mu}$ evolution have been provided in the appendix. It is important to note that the chain distribution may not remain as Gaussian for the entire deformation history (especially in the regime, when the chain end-to-end distance attends full contour length as $\mathbf{r} \rightarrow Nb$). For non-Gaussian distribution, simplification of $\boldsymbol{\mu}$ via a symmetric tensor is not possible. In the present study we assume that the chain distribution remains close

to Gaussian for the entire oxidation and deformation history and the kinetics of the chain association/dissociation events are independent of the mechanical force.

2.5. *A phase-field fracture model to predict macroscale damage and fracture in polymers due to oxidation*

In the previous section, we have proposed a method for predicting the microscale evolution of the network morphology depending on the oxidative reaction kinetics. In this section we propose a phase-field fracture theory to model macroscopic damage initiation and propagation in terms of cracks during a stress-coupled oxidative aging process. The final goal is to connect the reaction modified polymer network response with the macroscopic fracture originating due to stress inhomogeneity, during an oxidative aging process. The use of a phase-field fracture model would help in predicting the fracture initiation and modeling crack propagation in complex conditions such as mixed mode, interacting cracks, complex distribution of initiation sites etc., under a coupled physics driven scenario such as oxidative aging. The model builds upon a coupled mechanical and oxygen diffusion response, driven by the displacement boundary conditions and the chemical potential gradients. It further considers a reaction dependent amorphous polymer network with constantly evolving network morphology and mechanical properties .

2.5.1. *Phase-field order parameter or macroscale damage variable*

In the phase-field fracture theory, we define a phase-field order parameter or damage variable d such that,

$$0 \leq d(\mathbf{X}, t) \leq 1 \quad (26)$$

where $d = 0$ represents the material being intact and $d = 1$ corresponds to a fully broken material. Thus, the phase-field order parameter or damage variable interpolates between the broken state of the material and its unbroken state [2, 61, 63]. We assume that d monotonically increases, such that $\dot{d} \geq 0$, implying that the damage is irreversible. In

order to define a diffusive crack topology to approximate the non-smooth crack field, the phase-field theory introduces an exponential function for $d(\mathbf{X})$, as $d(\mathbf{X}, t) = e^{-\frac{\chi}{l_c}}$ [61–63]. The length scale parameter l_c is introduced to govern the regularization or the width of the diffusive zone and gives the sharp crack topology for $l_c \rightarrow 0$ (Fig. 2). The theory further considers dependence on d and the gradient ∇d to incorporate the spatial inhomogeneity due to localized damage formation.

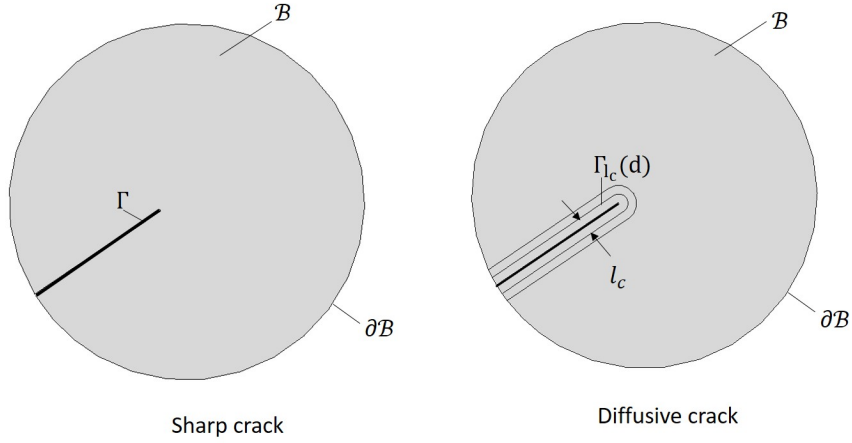


Figure 2: Sharp and diffusive crack topology: a sharp crack Γ embedded into the solid B (left) and the regularized crack surface Γ_c with a functional of crack phase field d and the crack regularization length l_c .

2.6. A Chemo-mechanically coupled thermodynamically consistent theory for polymer oxidation:- the balance laws

2.6.1. Mass balance for the diffusing and reacting species

Let P denotes any arbitrary domain of the body B_R in the reference configuration surrounded by the boundary ∂P . Let $c_R^\beta(\mathbf{X}, t)$ denotes the concentration of species β in moles per unit reference volume which takes part into the oxidation reactions. The changes in the concentration of c_R^β for any species β are caused by diffusion of that species across the boundary ∂P , which is characterized by a flux $\mathbf{j}_R^\beta(\mathbf{X}, t)$, defined by the number of diffusing species measured per unit area per unit time. Similarly, $r_R^\beta(\mathbf{X}, t)$ denotes the number of moles for

species β that is either consumed or produced per unit time due to the chemical reaction. The general mass balance law for any participating species β therefore takes the form,

$$\frac{d}{dt} \int_P c_R^\beta dv_R = - \int_{\partial P} \mathbf{j}_R^\beta \cdot \mathbf{n}_R da_R + \int_P r_R^\beta dv_R \quad (27)$$

for every part P ; where $\mathbf{n}_R$ represents a unit vector in the reference configuration. Bringing the time derivative in Eq. 27 inside the integral and using the divergence theorem on the integral over ∂P , we find that

$$\int_P (\dot{c}_R^\beta + \text{Div} \mathbf{j}_R^\beta - r_R^\beta) dv_R = 0 \quad (28)$$

Since P is arbitrary, this leads to the local form of mass balance as,

$$\dot{c}_R^\beta = -\text{Div} \mathbf{j}_R^\beta + r_R^\beta \quad (29)$$

Using Eq. 3 into 29, we can write,

$$\dot{c}_R^\beta = -\text{Div} \mathbf{j}_R^\beta + \sum_n [\mathcal{R}_{n\beta} \dot{\xi}_n] \quad (30)$$

We have assumed oxygen is the only diffusing species. Also from Eq. 1, O_2 is consumed in propagation reaction (II) and produced in termination reaction (VI). Hence, the mass balance equation for O_2 has the following form:

$$\dot{c}_R^{\text{O}_2} = -\text{Div} \mathbf{j}_R^{\text{O}_2} + \mathcal{R}_2 \dot{\xi}_2 + \mathcal{R}_6 \dot{\xi}_6 \quad (31)$$

For the other constituents, mass balance would involve only the reaction dependant changes as there is no diffusion, as given by [52] and re-written here. The balance of POOH concentration is thus given by,

$$\dot{c}_R^{\text{POOH}} = \mathcal{R}_1 \dot{\xi}_1 + \mathcal{R}_3 \dot{\xi}_3 \quad (32)$$

The rate of change of PH-concentration can be tracked as,

$$\dot{c}_R^{\text{PH}} = \mathcal{R}_3 \dot{\xi}_3 \quad (33)$$

The termination products due to oxidation are the carbonyls (POOP). We can write the mass balance for POOP as,

$$\dot{c}_R^{\text{POOP}} = \mathcal{R}_5 \dot{\xi}_5 + \mathcal{R}_6 \dot{\xi}_6 \quad (34)$$

2.6.2. Balance of forces and moments: Principle of virtual power

Using the principle of virtual power, we can derive the macroscopic and microscopic force balance conditions. Following similar notation as mentioned in [49], we consider the rate-like kinematical descriptors as $\dot{\boldsymbol{\chi}}$, $\dot{\mathbf{F}}$, $\dot{\xi}_n$, $\dot{d}$ and $\nabla \dot{d}$.

For the macroscopic force balance, we consider that, on the arbitrary part P of the reference body $\mathcal{B}_R$, there exists a traction force $\mathbf{t}_R(\mathbf{n}_R)$ that expends power over the velocity $\dot{\boldsymbol{\chi}}$. There also exists a stress tensor, $\mathbf{T}_R$ that expends power over the rate $\dot{\mathbf{F}}$ of the deformation gradient. Similarly, we consider a scalar microscopic stress ϖ , expending power over the rate of the damage variable, $\dot{d}$. Additionally, a vector microscopic stress $\boldsymbol{\zeta}$ is introduced that expends power over the gradient $\nabla \dot{d}$. Finally, there also exists a scalar microscopic traction $\zeta(\mathbf{n}_R)$ that expends power over $\dot{d}$ on the boundary of the part. Then we can write the external and internal power of the system as,

$$\mathcal{W}_{ext} = \int_{\partial P} \mathbf{t}_R(\mathbf{n}_R) \cdot \dot{\boldsymbol{\chi}} da_R + \int_P \mathbf{b}_R \cdot \dot{\boldsymbol{\chi}} dv_R + \int_{\partial P} \zeta(\mathbf{n}_R) \dot{d} da_R \quad (35)$$

$$\mathcal{W}_{int} = \int_P \left(\mathbf{T}_R : \dot{\mathbf{F}} + \varpi \dot{d} + \boldsymbol{\zeta} \cdot \nabla \dot{d} \right) dv_R \quad (36)$$

where $\mathbf{b}_R$ is the non-inertial body force per unit volume of the reference body. Introducing the virtual rate fields as $(\tilde{\boldsymbol{\chi}}, \tilde{\mathbf{F}}, \tilde{d}, \nabla \tilde{d})$, we can further write the external and internal expenditures of virtual power as,

$$\mathcal{W}_{ext,\mathcal{V}} = \int_{\partial P} \mathbf{t}_R(\mathbf{n}_R) \cdot \tilde{\boldsymbol{\chi}} da_R + \int_P \mathbf{b}_R \cdot \tilde{\boldsymbol{\chi}} dv_R + \int_{\partial P} \zeta(\mathbf{n}_R) \tilde{d} da_R \quad (37)$$

$$\mathcal{W}_{int,\mathcal{V}} = \int_P \left(\mathbf{T}_R : \tilde{\mathbf{F}} + \varpi \tilde{d} + \boldsymbol{\zeta} \cdot \nabla \tilde{d} \right) dv_R \quad (38)$$

Now the principle of virtual power requires that $\mathcal{W}_{ext,\mathcal{V}} = \mathcal{W}_{int,\mathcal{V}}$, and $\mathcal{W}_{int,\mathcal{V}} = 0$ for rigid virtual velocity $\mathcal{V}$, for any part P . The consequence of these requirements provides us the macroforce balance consistent with the Piola stress as,

$$\text{Div} \mathbf{T}_R + \mathbf{b}_R = \mathbf{0} \quad \text{and} \quad \mathbf{T}_R \mathbf{F}^T = \mathbf{F} \mathbf{T}_R^T \quad (39)$$

Eq. 39 represent the local macroforce and moment balance for the reference body. As is

standard, Piola stress is related to the symmetric Cauchy stress in the deformed body by,

$$\mathbf{T} = J^{-1} \mathbf{T}_R \mathbf{F}^T \quad (40)$$

And the microstresses $\boldsymbol{\zeta}$ and ϖ are consistent with the microforce balance equation together with the microtraction condition as:

$$\text{Div} \boldsymbol{\zeta} - \varpi = 0 \quad \text{and} \quad \boldsymbol{\zeta}(\mathbf{n}_R) = \boldsymbol{\zeta} \cdot \mathbf{n}_R \quad (41)$$

2.6.3. Energy imbalance

Let us consider an *isothermal polymer oxidation* process in any arbitrary part P of a reference body B_R . Neglecting the inertia effect, the internal energy in P can be written as less than or equal to the power expended on the part due to chemical reactions, damages etc. plus the energy increase due to change in concentration in the species due to the diffusion. Thus, denoting ψ_R as the internal energy density per unit volume of the reference body, we can write the energy imbalance as,

$$\overline{\int_P \dot{\psi}_R dv_R} \leq \int_{\partial P} \mathbf{t}_R \mathbf{n}_R \cdot \dot{\boldsymbol{\chi}} da_R + \int_P \mathbf{b}_R \cdot \dot{\boldsymbol{\chi}} dv_R + \int_{\partial P} (\boldsymbol{\zeta} \cdot \mathbf{n}_R) \dot{d} da_R - \sum_{\beta} \int_{\partial P} \mu^{\beta} \mathbf{j}_R^{\beta} \cdot \mathbf{n}_R da_R \quad (42)$$

where μ^{β} is the chemical potential for any species β and $\mu^{\beta} \mathbf{j}_R^{\beta}$ is the energy carried by species β into part P by the flux $\mathbf{j}_R^{\beta}$. Applying divergence theorem to the terms on the integrals over ∂P and bringing the time derivative inside the integral, Eq. 42 can be re-written as,

$$\begin{aligned} \int_P \dot{\psi}_R dv_R \leq & \int_P \left(\mathbf{T}_R : \dot{\mathbf{F}} + \text{Div} \mathbf{T}_R \cdot \dot{\boldsymbol{\chi}} \right) dv_R + \int_P \mathbf{b}_R \cdot \dot{\boldsymbol{\chi}} dv_R + \int_P \left(\text{Div} \boldsymbol{\zeta} \dot{d} + \boldsymbol{\zeta} \cdot \nabla \dot{d} \right) dv_R \\ & - \sum_{\beta} \int_P \left(\mu^{\beta} \text{Div} \mathbf{j}_R^{\beta} + \mathbf{j}_R^{\beta} \cdot \nabla \mu^{\beta} \right) dv_R \quad (43) \end{aligned}$$

Reorganizing Eq. 43, we have,

$$\begin{aligned} \int_P \dot{\psi}_R dv_R \leq & \int_P \left(\mathbf{T}_R : \dot{\mathbf{F}} + \boldsymbol{\zeta} \cdot \nabla \dot{d} - \sum_{\beta} [\mu^{\beta} \text{Div} \mathbf{j}_R^{\beta} + \mathbf{j}_R^{\beta} \cdot \nabla \mu^{\beta}] \right) dv_R + \\ & \int_P (\text{Div} \mathbf{T}_R + \mathbf{b}_R) \cdot \dot{\boldsymbol{\chi}} dv_R + \int_P (\text{Div} \boldsymbol{\zeta}) \dot{d} dv_R \quad (44) \end{aligned}$$

Using Eq. 30, 41, and 39 in Eq. 44 and considering P as arbitrary, we could write the local form of energy balance as,

$$\dot{\psi}_R - \mathbf{T}_R : \dot{\mathbf{F}} - \varpi \dot{d} - \boldsymbol{\zeta} \cdot \nabla \dot{d} + \sum_{\beta} \mathbf{j}_R^{\beta} \cdot \nabla \mu^{\beta} + \sum_{\beta} \mu^{\beta} \sum_n [\mathcal{R}_{n\beta} \dot{\xi}_n] - \sum_{\beta} \mu^{\beta} \dot{c}_R^{\beta} \leq 0 \quad (45)$$

Since the stress measure $\mathbf{T}_R$ is not symmetric, we introduce the 2nd PK stress $\mathbf{S}$ and its conjugate right Cauchy-Green strain $\mathbf{C}$ to express the stress power as,

$$\mathbf{T}_R : \dot{\mathbf{F}} \equiv \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} \quad (46)$$

and Eq. 45 can be finally written as,

$$\dot{\psi}_R - \mathbf{S} : \frac{1}{2} \dot{\mathbf{C}} - \varpi \dot{d} - \boldsymbol{\zeta} \cdot \nabla \dot{d} + \sum_{\beta} \mathbf{j}_R^{\beta} \cdot \nabla \mu^{\beta} + \sum_{\beta} \mu^{\beta} \sum_n [\mathcal{R}_{n\beta} \dot{\xi}_n] - \sum_{\beta} \mu^{\beta} \dot{c}_R^{\beta} \leq 0 \quad (47)$$

2.6.4. Basic constitutive equations

In this Section, we consider a theory which allows for an energetic and dissipative effects associated with the temporal changes in d , and also an energetic effect due to the gradient ∇d . We consider the gradient ∇d as a measure of the inhomogeneity due to localized damage formation. We also consider that scalar microstress, ϖ , can be broken down into an energetic and dissipative part respectively, based on the similar approach proposed in [6, 67] as,

$$\varpi = \varpi_{en} + \varpi_{dis} \quad (48)$$

Guided by the free energy imbalance Eq. 45, a functional form is assumed for the free energy $\psi_R = \hat{\psi}_R(\mathbf{\Lambda})$, where $\mathbf{\Lambda} = (\mathbf{C}, c_R^{\beta}, \xi_n, d, \nabla d)$; the second Piola stress $\mathbf{S}$, vector microstress $\boldsymbol{\zeta}$ and the chemical potential of species μ^{β} are then determined by the constitutive equations of the form,

$$\mathbf{S} = \hat{\mathbf{S}}(\mathbf{\Lambda}), \quad \mu^{\beta} = \hat{\mu}^{\beta}(\mathbf{\Lambda}), \quad \boldsymbol{\zeta} = \hat{\boldsymbol{\zeta}}(\mathbf{\Lambda}) \quad (49)$$

Further, the species flux $\mathbf{j}_R^{\beta}$ can be assumed to have the following constitutive form:

$$\mathbf{j}_R^{\beta} = \hat{\mathbf{j}}_R^{\beta}(\mathbf{\Lambda}) \quad (50)$$

Then, by invoking the thermodynamic restrictions it is possible to generate the specific forms for the constitutive equations.

Thermodynamic restrictions:- Following Eq. 49, we get

$$\dot{\psi}_R = \frac{\partial \hat{\psi}_R}{\partial \mathbf{C}} : \dot{\mathbf{C}} + \frac{\partial \hat{\psi}_R}{\partial d} \dot{d} + \frac{\partial \hat{\psi}_R}{\partial \nabla d} \cdot \nabla \dot{d} + \sum_{\beta} \frac{\partial \hat{\psi}_R}{\partial c_R^{\beta}} \dot{c}_R^{\beta} + \sum_n \frac{\partial \hat{\psi}_R}{\partial \xi_n} \dot{\xi}_n \quad (51)$$

In view of Eq. 51, the free energy imbalance Eq. 45 is equivalent to the requirement that the following inequality must be satisfied for all the constitutive processes:

$$\begin{aligned} \left(\frac{\partial \hat{\psi}_R}{\partial \mathbf{C}} - \frac{1}{2} \hat{\mathbf{S}} \right) : \dot{\mathbf{C}} + \left(\frac{\partial \hat{\psi}_R}{\partial d} - \varpi \right) \dot{d} + \left(\frac{\partial \hat{\psi}_R}{\partial \nabla d} - \boldsymbol{\zeta} \right) \cdot \nabla \dot{d} + \sum_{\beta} \left(\frac{\partial \hat{\psi}_R}{\partial c_R^{\beta}} - \hat{\mu}^{\beta} \right) \dot{c}_R^{\beta} \\ - \left[\left(- \sum_{\beta} \mu^{\beta} \sum_n \mathcal{R}_{n\beta} - \sum_n \frac{\partial \hat{\psi}_R}{\partial \xi_n} \right) \dot{\xi}_n \right] + \sum_{\beta} \hat{\mathbf{j}}_R^{\beta} \cdot \nabla \mu^{\beta} \leq 0 \end{aligned} \quad (52)$$

To hold the above equation true for any arbitrary $\dot{\mathbf{C}}$, $\dot{c}_R^{\beta}$ and $\nabla \dot{d}$, their coefficients must vanish. Therefore, we can get the 2nd P-K stress, $\mathbf{S}$, the microstress, $\boldsymbol{\zeta}$ and the chemical potential, μ^{β} as,

$$\mathbf{S} = 2 \frac{\partial \psi_R(\boldsymbol{\Lambda})}{\partial \mathbf{C}}; \quad \mu^{\beta} = \frac{\partial \psi_R(\boldsymbol{\Lambda})}{\partial c_R^{\beta}} \quad (53)$$

We also consider the vector microstress $\boldsymbol{\zeta}$ as energetic, and thus,

$$\boldsymbol{\zeta} = \frac{\partial \psi_R(\boldsymbol{\Lambda})}{\partial \nabla d} \quad (54)$$

We define the energetic microstress ϖ_{en} as,

$$\varpi_{en} = \frac{\partial \psi_R(\boldsymbol{\Lambda})}{\partial d} \quad (55)$$

so that the dissipative microstress ϖ_{dis} can be written as,

$$\varpi_{dis} = \varpi - \varpi_{en} \quad (56)$$

The species flux satisfies the species-transport inequality as,

$$\hat{\mathbf{j}}_R^{\beta}(\boldsymbol{\Lambda}) \cdot \nabla \mu^{\beta} \leq 0 \quad (57)$$

In this work, we assume that the fluid flux obeys Fick's law, i.e. the flux depends linearly on the gradient of the chemical potential and thus can be expressed by,

$$\hat{\mathbf{j}}_R^{\beta} = -\mathbf{M}^{\beta} \nabla \mu^{\beta} \quad (58)$$

with $\mathbf{M}^\beta$ is the mobility tensor. Substituting Eq. 58 into 57, we get the species-transport inequality as,

$$\nabla \mu^\beta \cdot \mathbf{M}(\boldsymbol{\Lambda}) \nabla \mu^\beta \geq 0 \quad (59)$$

Hence, we are finally left with the following dissipation inequality:-

$$\varpi_{dis} \dot{d} + \left[\left(- \sum_{\beta} \mu^\beta \sum_n \mathcal{R}_{n\beta} - \sum_n \frac{\partial \hat{\psi}_R}{\partial \xi_n} \right) \dot{\xi}_n \right] \geq 0 \quad (60)$$

We assume that each individual term of Eq. 60 satisfies the dissipation inequalities as:

$$\begin{cases} \varpi_{dis} \dot{d} \geq 0 \\ \left(- \sum_{\beta} \mu^\beta \sum_n \mathcal{R}_{n\beta} - \sum_n \frac{\partial \hat{\psi}_R}{\partial \xi_n} \right) \dot{\xi}_n \geq 0, \end{cases} \quad (61)$$

From Eq. 61, we consider that ϖ_{dis} is the driving force for the phase-field damage d .

In addition, from the chemistry literature, we know that there exists a quantity called *affinity*, $\mathcal{A}_n$, which is the driving force equivalent, as,

$$\mathcal{A}_n = - \frac{\partial \psi_R}{\partial \xi_n} \quad (62)$$

Hence, it is possible to define a force of dissipative nature $\mathcal{F}_n$ which is a conjugate to $\dot{\xi}_n$ for each reaction n . Thus,

$$\mathcal{F}_n = \mathcal{A}_n - \sum_{\beta} \mu^\beta \mathcal{R}_{n\beta}, \quad (63)$$

This reflects the fact that every chemical reaction relates to a dissipative mechanism. The extent of reaction for any reaction ξ_n is assumed to evolve according to a state relation

$$\dot{\xi}_n = \hat{\xi}_n(\mathcal{F}_n, \vartheta, \xi_n, c_R^\beta) \geq 0 \quad (64)$$

with $\mathcal{F}_n \dot{\xi}_n > 0$, whenever $\dot{\xi}_n > 0$, and ϑ is the reference temperature.

2.7. Specialization of the constitutive equations

For deriving the specific constitutive forms, we consider the materials as initially and continually isotropic. Under such assumption, it can be shown that the response of the polymer is invariant under any arbitrary rotation in the reference configuration or intermediate configuration and the constitutive responses do not change [3–5, 22, 23, 56].

To simplify the numerical implementation, we consider a Gent hyperelastic free energy function for the mechanical part [43]. It is important to note that the Gent free energy accounts for the limiting chain extensibility in a phenomenological way. However, its statistical basis can be proved based on an approximation of molecular based average stretch for the full network, as reported in [51].

For the chemical part of the free energy, a simple quadratic function of the extent of reaction (ξ_n) is considered, (based on the recent literature [52, 56, 75, 84]). Following the formulation in [52], we have assumed only oxygen diffusion takes place within the polymer during oxidation. Hence, the free energy for the diffusion is considered as the energy of mixing between the diffused oxygen and the polymer. Polymer being the long-chain macromolecules and the size of the diffused oxygen molecules being significantly smaller, Flory-Huggin's theory of mixing seems to be better suited to model the diffusive free energy [55, 77, 78]. Hence, we use a similar expression for diffusive free energy as used in earlier works of fluid diffusion in the polymers ([22–24, 41]).

It is important to note that as the phase-field damage progresses, the stored or mechanical energy of the material continues to degrade. In order to model that, we incorporate a widely used degradation function $g(d)$ as reported in the phase-field literature [6, 59, 61, 63, 67]. The function $g(d)$ is a monotonically decreasing function in d and it satisfies:- $g(0) = 1$, $g(1) = 0$, $g'(d) \leq 0$ and $g'(1) = 0$. We use the most common form for degradation function used in the literature [6, 61, 63, 67], as,

$$g(d) = (1 - d)^2 + \kappa \quad (65)$$

where κ is a small positive-valued constant which is introduced to prevent ill-conditioning of the model when $d = 1$.

Free energies:- Motivated by the free energy representation in [6], we consider that the free energy can be written in a separable form constituted of mechanical energy, chemical energy, energy of mixing and the fracture energy.

$$\hat{\psi}_R(\mathbf{C}, c_R^\beta, \xi_n, d, \nabla d) = g(d)\psi_R^{\text{mech}}(\mathbf{C}) + \psi_R^{\text{chem}}(\xi_n) + \psi_R^{\text{diff}}(c_R^{\text{O}_2}) + \psi_R^{\text{frac}}(d, \nabla d) \quad (66)$$

Mechanical free energy :- In what follows, we write the mechanical free energy following Gent hyperelastic model [43] in terms of the average stretch as,

$$\psi_R^{mech}(\bar{\lambda}, J) = -\frac{1}{2}G_{shear}\lambda_L \ln\left(1 - \frac{3(\bar{\lambda}^2 - 1)}{\lambda_L}\right) + \frac{K_{bulk}}{2}(J - 1)^2 \quad (67)$$

where, we have used the 1st strain invariant as, $I_1 = 3\bar{\lambda}^2 = tr(\mathbf{C})$, $J = det(\mathbf{F})$, the shear modulus G_{shear} varies as a function of c_{rc} , K_{bulk} is the bulk modulus of the polymer and λ_L is the limiting stretchability, dependent on c_{rd} .

Chemical energy :- ψ_R^{chem} is the reactive part of the free energy influencing the oxidation reaction and is given by,

$$\psi_R^{chem} = \sum_n \frac{H_n}{2}(1 - \xi_n)^2 \quad (68)$$

where the parameter H_n is the chemistry modulus of reaction n . This term in the free energy favors the local state ($\xi_n = 1$) [84].

Energy driving the diffusion of oxygen:- ψ_R^{diff} is the part of free energy involved in the diffusion of oxygen (O_2) into the polymer. As mentioned we have Flory-Huggins free energy to define the energy for diffusion [22–24, 41] as given by,

$$\psi_R^{diff} = \mu_0^{O_2} c_R^{O_2} + R\vartheta c_R^{O_2} \left[\ln\left(\frac{\Omega c_R^{O_2}}{1 + \Omega c_R^{O_2}}\right) + \chi \left(\frac{1}{1 + \Omega c_R^{O_2}}\right) \right] \quad (69)$$

where $\mu_0^{O_2}$ is the reference chemical potential for oxygen, R is the universal gas constant, ϑ is the temperature, χ is the dimensionless Flory-Huggins interaction parameter, and Ω is the volume of a mole of oxygen.

Fracture energy :- The free energy for the fracture is also considered as a quadratic form,

$$\psi_R^{frac} = \frac{G_c(c_{rd})l_c}{2} |\nabla d|^2 \quad (70)$$

where $G_c(c_{rd})$ is the Griffith-like fracture energy that evolves as a function of chain dissociation ratio, c_{rd} .

Thus the complete free energy expression can now be written as,

$$\begin{aligned} \hat{\psi}_R = g(d) & \left[-\frac{1}{2}G_{shear}\lambda_L \ln \left(1 - \frac{3(\bar{\lambda}^2 - 1)}{\lambda_L} \right) + \frac{K_{bulk}}{2}(J - 1)^2 \right] + \\ & \sum_n \frac{H_n}{2}(1 - \xi_n)^2 + \mu_0^{O_2} c_R^{O_2} + R\vartheta c_R^{O_2} \left[\ln \left(\frac{\Omega c_R^{O_2}}{1 + \Omega c_R^{O_2}} \right) + \chi \left(\frac{1}{1 + \Omega c_R^{O_2}} \right) \right] + \frac{G_c l_c}{2} |\nabla d|^2 \end{aligned} \quad (71)$$

Evolution equation for the phase-field variable d :- Based on Eq. 55, we can write the energetic microstress as,

$$\varpi_{en} = \frac{\partial \psi_R}{\partial d} = -2(1 - d)\psi_R^{mech} \quad (72)$$

where, ψ_R^{mech} is the mechanical free energy of the reaction modified polymer network, but without any macroscopic damage.

To determine the expression for ϖ_{dis} , let us consider the recent phase-field literature [61, 63], where the energy required to create a new fracture surface was given by,

$$\psi_s = \int_P G_c \left(\frac{1}{2l_c} d^2 + \frac{1}{2} l_c |\nabla d|^2 \right) dV \quad (73)$$

In order to be consistent with the energy dissipated to create new surface (as the first term in Eq. 73), we define the dissipative microstress as,

$$\varpi_{dis} = \frac{G_c(c_{rd})}{l_c} \quad (74)$$

It is important to recall that the modification of the Griffith energy would occur due to the chain scissions occurring in the polymer network during oxidation, as mentioned in Sec.2.3.2. Therefore, Eq. 48 can be re-written as,

$$\varpi = \varpi_{en} + \varpi_{dis} = -2(1 - d)\psi_R^{mech} + \frac{G_c}{l_c} \quad (75)$$

Further following Eq. 53, we can derive the vector microstress ζ as,

$$\zeta = G_c l_c \nabla d \quad (76)$$

Substituting Eq. 75 and 76 into the microstress balance Eq. 41 yields the evolution equation for d as,

$$2(1 - d)\psi_R^{mech} - \frac{G_c}{l_c} + G_c l_c \Delta d = 0 \quad (77)$$

where Δd represents the Laplacian of d . It is important to note that the evolution of d in Eq. 77 does not ensure the irreversibility constraint of the damage ($\dot{d} \geq 0$). In order to ensure the irreversibility condition, we can rewrite Eq. 77 while neglecting the gradient effect (∇d) on the damage variable as,

$$2(1-d) \left[\psi_R^{mech} - \frac{G_c}{2l_c} \right] - \frac{G_c}{l_c} d = 0 \quad (78)$$

It can be shown, that a monotonically increasing evolution of d requires the the term $(\psi_R^{mech} - \frac{G_c}{2l_c})$ to be strictly positive for the entire deformation history, [6, 61, 63, 67, 79]. Based on that a monotonically increasing history field $\mathcal{H}$ is introduced as,

$$\mathcal{H}(t) = \max_{s \in [0, t]} \left| \psi_R^{mech}(s) - \frac{G_c(s)}{2l_c} \right| \quad (79)$$

So that the evolution equation has the final form as,

$$2(1-d)\mathcal{H} - \frac{G_c}{l_c} d + G_c l_c \Delta d = 0 \quad (80)$$

Stress, chemical potential and affinity:- From the free energy expression Eq. 71 and using the guidelines for thermodynamic restriction, it is possible to get the specific constitutive forms for the Piola stress $\mathbf{T}_R$, chemical potential of oxygen, μ^{O_2} and affinity of each reaction, $\mathcal{A}_n$. The Piola stress can be expressed in the following form:

$$\mathbf{T}_R = J^{-2/3} g(d) \left[G_{shear} \left(1 - \frac{tr(\mathbf{C}) - 3}{\lambda_L} \right)^{-1} [\mathbf{F} - \frac{1}{3}(tr(\mathbf{C})\mathbf{F}^{-T}) + K_{bulk}J(J-1)\mathbf{F}^{-T}] \right] \quad (81)$$

where $tr(\mathbf{C})$ can be related to the average macroscopic stretch as $tr(\mathbf{C}) = 3\bar{\lambda}^2$, which can further be related to $\boldsymbol{\mu}$ as explained before; the shear modulus G_{shear} and the limiting stretchability λ_L are functions of c_{rc} and c_{rd} , respectively.

Chemical potential driving the diffusion of O_2 , μ^{O_2} , can be obtained by taking the partial derivative of the diffusive energy with respect to oxygen concentration as,

$$\mu^{O_2} = \mu_0^{O_2} + R\vartheta \left(\ln \left(\frac{\Omega c_R^{O_2}}{1 + \Omega c_R^{O_2}} \right) + \frac{1}{1 + \Omega c_R^{O_2}} + \chi \left(\frac{1}{1 + \Omega c_R^{O_2}} \right)^2 \right) \quad (82)$$

Finally, the affinity of any reaction n can be calculated from Eq. 62 and 71 as,

$$\mathcal{A}_n = H_n(1 - \xi_n) \quad (83)$$

Evolution of extent of reaction ξ_n : Based on the kinetics of chemical reaction for polymer oxidation and our discussion in section 2.1, we choose a thermally activated relation for the evolution of extent of reaction $\dot{\xi}_n$ as,

$$\dot{\xi}_n = k_n \exp\left(\frac{-Q_{act}^n}{R\vartheta}\right) \mathcal{F}_n \quad (84)$$

where, k_n is the pre-exponential rate constant for reaction n and has an unit of $\frac{1}{MPa-s}$, Q_{act}^n is the activation energy for reaction n .

As explained earlier, reaction would occur only when $\mathcal{F}_n > 0$. Further, the reaction would be considered as completed when the extent of reaction reaches unity. Following this, we can rewrite Eq. 84 as,

$$\dot{\xi}_n = \begin{cases} k_n \exp\left(\frac{-Q_{act}^n}{R\vartheta}\right) \mathcal{F}_n, & \text{when } \mathcal{F}_n > 0 \text{ and } \xi_n < 1 \\ 0, & \text{otherwise} \end{cases} \quad (85)$$

Oxygen flux and diffusivity:- From Eq. 58, oxygen flux is given by,

$$\mathbf{j}_R^{O_2} = -m^{O_2} \nabla \mu^{O_2} \quad (86)$$

with m^{O_2} being the mobility of oxygen. Ignoring the effect of temperature gradient we can write from Eq. 82,

$$\nabla \mu^{O_2} = \frac{R\vartheta}{c_R^{O_2}} \left(\frac{1}{1 + \Omega c_R^{O_2}} - \frac{\Omega c_R^{O_2}}{(1 + \Omega c_R^{O_2})^2} - 2\chi \frac{\Omega c_R^{O_2}}{(1 + \Omega c_R^{O_2})^3} \right) \nabla c_R^{O_2} \quad (87)$$

Further, diffusivity of oxygen can be defined as,

$$D = m^{O_2} \times \frac{R\vartheta}{c_R^{O_2}} \quad (88)$$

Using Eq. 88 in 86 the constitutive relation for oxygen flux can be obtained as,

$$\mathbf{j}_R^{O_2} = -D \left(\frac{1}{1 + \Omega c_R^{O_2}} - \frac{\Omega c_R^{O_2}}{(1 + \Omega c_R^{O_2})^2} - 2\chi \frac{\Omega c_R^{O_2}}{(1 + \Omega c_R^{O_2})^3} \right) \nabla c_R^{O_2} \quad (89)$$

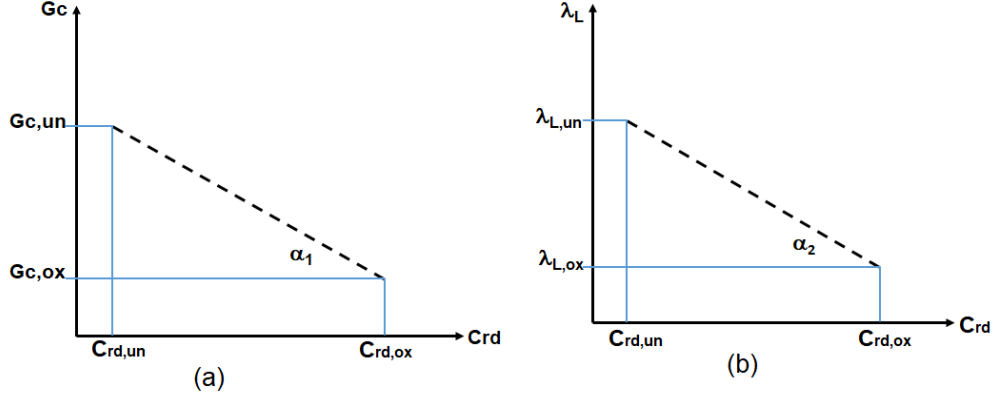


Figure 3: Linear trend of fracture energy and limiting chain stretchability parameter as a function of dissociated chain ratio

Reaction dependent shear modulus, fracture energy and limiting chain extensibility parameters:- According to the description in section 2.3.2, we assume that, shear modulus is directly proportional to the active chain ratio and can be written as,

$$G_{shear}(c_{rc}) = c_{rc}G_0 = c_{rc}c(t_0)k_B\vartheta \quad (90)$$

where G_0 is the virgin shear modulus of the material which is a function of active chain concentration at virgin state $c(t_0)$, and k_B is the Boltzmann constant.

Fracture energy (G_c) and the limiting chain stretchability parameter (λ_L) have been considered as degrading linearly with the dissociated chain ratio (as shown schematically in Fig 3), characterizing the increase in brittleness due to oxidative scissions in the network. Thus, we define the reaction dependent fracture energy via a linear relation as,

$$G_c(c_{rd}) = \alpha_1 c_{rd} + C_1 \quad (91)$$

with $\alpha_1 = \frac{G_{c,ox} - G_{c,un}}{c_{rd,ox} - c_{rd,un}}$ and $C_1 = [G_{c,ox} + G_{c,un} - \alpha_1(c_{rd,ox} - c_{rd,un})]/2$; where $G_{c,ox}$ and $G_{c,un}$ are the fracture energy at completely oxidized and virgin state respectively, and $c_{rd,ox}$ and $c_{rd,un}$ are the corresponding dissociated chain ratios.

Similarly, we define the limiting chain extensibility parameter as,

$$\lambda_L(c_{rd}) = \alpha_2 c_{rd} + C_2 \quad (92)$$

where, $\alpha_2 = \frac{\lambda_{L,ox} - \lambda_{L,un}}{c_{rd,ox} - c_{rd,un}}$ and $C_2 = [\lambda_{L,ox} + \lambda_{L,un} - \alpha_2(c_{rd,ox} - c_{rd,un})]/2$; with $\lambda_{L,ox}$ and $\lambda_{L,un}$ are the stretchability at completely oxidized and virgin state respectively,.

2.8. Governing differential equations and the boundary conditions

There are three governing partial differential equations required to be solved in this case:

$$\begin{cases} \text{Div} \mathbf{T}_R + \mathbf{b}_R = \mathbf{0} \\ \dot{c}_R^{O_2} = -\text{Div} \mathbf{j}_R^{O_2} + \mathcal{R}_2 \dot{\xi}_2 + \mathcal{R}_6 \dot{\xi}_6 \\ 2(1-d)\mathcal{H} - \frac{G_c}{l_c}d + G_c l_c \Delta d = 0 \end{cases} \quad (93)$$

We require the initial and boundary conditions to complete the solutions of these differential equations. Let, S_1 and S_2 are complementary subsurfaces of the boundary ∂B_R of a reference body B_R such that $S_1 \cup S_2 = \partial B_R$ and $S_1 \cap S_2 = \emptyset$. Similarly, let S_{c_R} and S_{j_R} are complementary subsurfaces of the boundary $\partial B_R = S_{c_R} \cup S_{j_R}$ with $S_{c_R} \cap S_{j_R} = \emptyset$. Lastly, we consider that, there exist two complementary surfaces S_d and S_ζ of the boundary such that $\partial B_R = S_d \cup S_\zeta$ with $S_d \cap S_\zeta = \emptyset$. For a time interval $t \in [0, T]$, three boundary conditions can be described such that displacement is known on S_1 and traction on S_2 . Thus, we can write,

$$\begin{aligned} \chi &= \check{\chi} \text{ on } S_1 \quad \forall t \in [0, T] \\ \mathbf{T}_R \mathbf{n}_R &= \check{\mathbf{t}}_R \text{ on } S_2 \quad \forall t \in [0, T] \end{aligned} \quad (94)$$

Similarly, another pair of boundary condition can be considered for a time interval $t \in [0, T]$ such that oxygen concentration is known on S_{c_R} and oxygen flux on S_{j_R} and thus,

$$\begin{aligned} c_R^{O_2} &= \check{c}_R \text{ on } S_{c_R} \quad \forall t \in [0, T] \\ -(\mathbf{j}_R) \cdot \mathbf{n}_R &= \check{j}_R \text{ on } S_{j_R} \quad \forall t \in [0, T] \end{aligned} \quad (95)$$

Finally, the boundary conditions for the evolution of d are,

$$\begin{aligned} d &= 0 \text{ on } S_d \quad \forall t \in [0, T] \\ (\nabla d) \cdot \mathbf{n}_R &= 0 \text{ on } S_\zeta \quad \forall t \in [0, T] \end{aligned} \quad (96)$$

The initial conditions are,

$$\chi(\mathbf{X}, 0) = \chi_0, \text{ and } c_R(\mathbf{X}, 0) = c_R^0 \text{ and } d(\mathbf{X}, 0) = 0 \text{ in } B_R. \quad (97)$$

Thus the coupled set of equations, Eq. 93, together with 94, 95 and 97 pose an initial boundary value problem to be solved for the displacement $\chi(\mathbf{X}, t)$, oxygen concentration $c_R^{O_2}(\mathbf{X}, t)$ and phase field parameter d simultaneously. In this work, the system of equations are solved numerically by writing a user element subroutine (UEL) in ABAQUS/Standard (2017) [1].

3. Material Parameter Estimation

To numerically implement the present theory, a number of material parameters are required for modeling the coupled behavior of multiple chemical reactions-diffusion, large deformation and phase field fracture in polymer. Estimation of the kinetic parameters for the diffusion and chemical reactions has been explained in detail in our previous work [52]. Hence, we ignore that part here for the sake of brevity. The kinetic parameters used in the present work are listed in B.2.

As described in Section 2.3.2, chemical reactions in the oxidation process cause chain-scissions (associated with the rate coefficient k_d) and oxidative crosslinking (associated with the rate coefficient k_a); which in turn, leads to the evolution of the active chain concentration and chain distribution. In order to determine these rate-like reaction dependent coefficients we have used experimental data as reported in [39]. A simple curve fitting procedure is adopted assuming an exponential relation between the concentration data for chain-scissions and crosslinks as a function of oxidation time, as shown in Fig. 4. As evident from the data in [39], the chain-scission phenomenon essentially dominates over the oxidative crosslinking in this typical thermoplastic polymer. On the other hand, crosslinking event could be more prominent in the case of some typical thermosets during oxidation as reported in [35–37].

Thermo-oxidative aging significantly affects the critical strain energy release rate or the fracture toughness (G_c) of the material, reducing it by two or three orders of magnitude as reported in [38, 39]. As identified, the chain-scission mechanism destroys the polymer

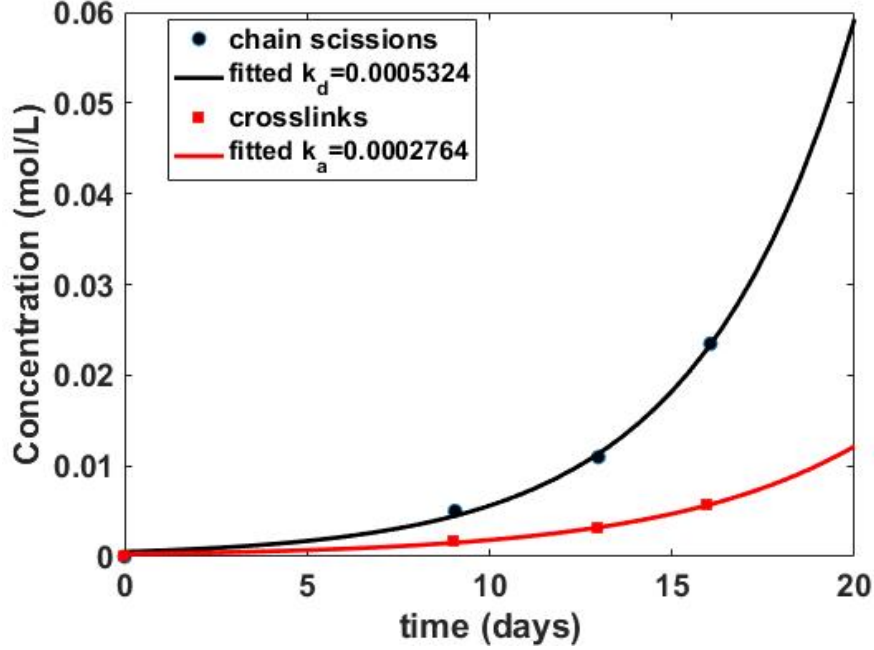


Figure 4: Estimation for the k_a and k_d , the rate-like coefficients for polyethylene; the "markers" correspond to the experimental data from [39].

network structure to a point where plastic deformation process do not initiate and hence the embrittlement occurs [39]. In this work we choose a Griffith-like fracture energy release rate as 1.44 kN/mm for virgin polymer and 10 N/mm for a completely oxidized polymer, consistent with the values as reported in the literature [38], for a typical polymer.

The other parameter to describe the mechanical free energy of the polymer network is the limiting chain extensibility (λ_L). Oxidative embrittlement process notably reduces the ultimate failure strain of the material, as the stretchability drops from a value of 800% to 10% as observed in the case of oxidative aging of polypropylene, [38]. For the present simulation, we use $\lambda_L = 3.0$ for the unoxidized polymer and $\lambda_L = 1.9$ for the completely oxidized polymer. The G_c and λ_L values used in the simulations are tabulated in the appendix (Table B.1).

4. Representative numerical simulations

4.1. Case study-1: Oxidative aging of a dogbone specimen followed by tensile loading

In this example, we numerically simulate the oxidative aging of a representative polymer dogbone specimen followed by a tensile testing to imitate a typical oxidation experiment performed in a laboratory setting. In the simulation, we consider the initial shear modulus as $G_0 = 0.58\text{GPa}$ and a final oxidized modulus as $G_{shear,ox} = 0.7\text{ GPa}$. The other important mechanical and kinetic parameters are as listed in Table B.1 and B.2 respectively. The geometry of the dogbone sample and the corresponding FE mesh have been shown in Fig. 5(a). Due to the symmetry, we analyze only one-quarter of the sample using 2D plane strain elements and apply symmetric boundary conditions along the mid-planes in the x and y-directions. The length scale parameter to describe the diffuse damage zone has been chosen as, $l_c = 500\mu m$. In a traditional lab environment, a sample is first oxidized within an oven at a temperature close or higher than the glass transition temperature of the material for several hours. Subsequently, it is taken out to perform mechanical testings to determine the effect of oxidation on the material's response. In what follows, we perform a two-step simulation where at first we let the sample to be oxidized at $80^\circ C$ for several hours in an accelerated aging environment. In the second step, we pull the sample at a displacement rate of $2.5 \times 10^{-5}\text{ mm/s}$ until the final failure happens. The corresponding chemical and mechanical boundary conditions are shown in Fig. 5(b). In the first step, we consider that, the sample surface is surrounded by a constant flow of O_2 with partial pressure of 2 atm, which translates to a constant O_2 concentration of $2.8 \times 10^{-2}\text{ mol/L}$. In order to avoid convergence issue, we have applied the chemical boundary condition in a ramp-like manner over a small time period of 2 hours. In the following step, we have applied the displacement boundary condition on the top surface of the specimen in a ramp-like manner as well (Fig. 5(b)). Our aim is to study the effect of oxidative aging in terms of the mechanical property degradation upon oxidizing the sample for 30, 50 and 100 hours, respectively. We consider two specific cases to understand the kinetics of the chains- i) when chain scission rate is dominant over the reattachment rate ($k_a < k_d$) and ii) when the chain reattachment is higher ($k_a > k_d$)

compared to the scission rate. Since oxidation is a time-dependent process, longer exposure to oxidative environment inevitably leads to the higher values of the extent of reactions, which, in turn, yields harsher property degradation, as demonstrated in the simulations results, as discussed in the following paragraph.

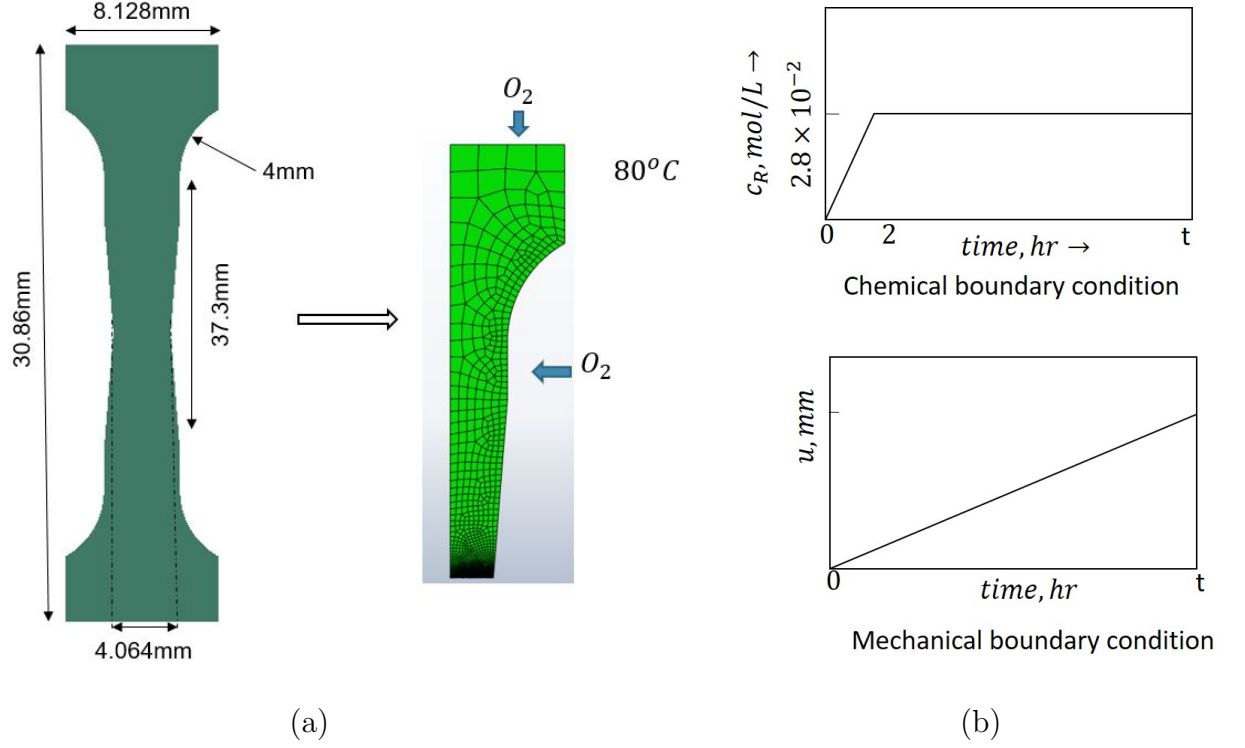


Figure 5: (a) Geometry and corresponding 2D plain strain finite element mesh of a dogbone specimen; (b) boundary condition for the oxygen concentration applied at the edges of the dogbone sample (top) and the displacement boundary condition applied at the top surface of specimen in Step-2 (bottom).

Fig. 6(a) and (b) show the contour plots of extent of reaction (III) (ξ_3) and extent of reaction (VI) (ξ_6) at the end of 30 hours (left), 50 hours (middle) and 100 hours (right), respectively. The corresponding changes in G_{shear} and λ_L are shown in Fig. 7 and Fig. 8, respectively. The extent of reactions monotonically increase in a continuous oxidation process. As time progresses, the evolution of ξ_3 leads to resin depletion by breaking the PH-chains and formation of some new hydro-peroxides (POOH). On the other hand, the termination reaction

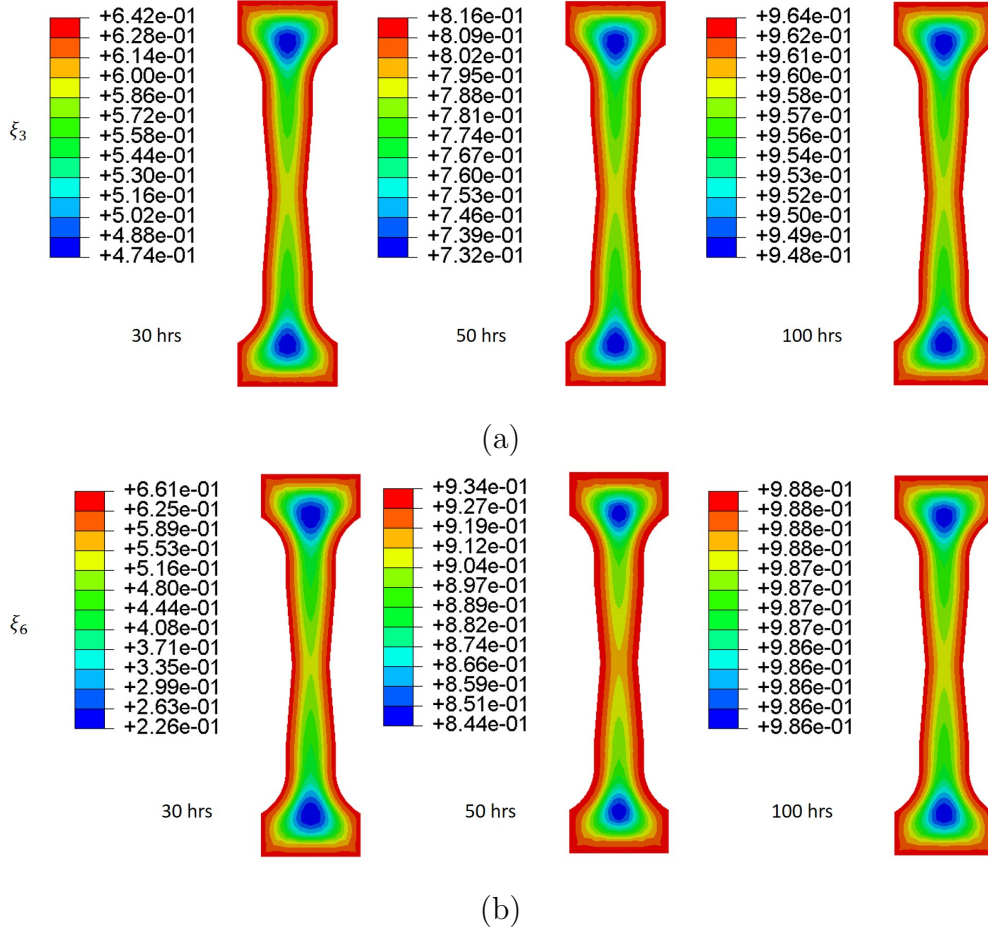


Figure 6: Contour plots for (a) extent of reaction ξ_3 after 30 hours (left), 50 hours (middle) and 100 hours (right); (b) extent of reaction ξ_6 after 30 hours (left), 50 hours (middle) and 100 hours (right).

(VI), ξ_6 forms new PO-OP bonds and these new bonds accumulate within the material as the reactions progress. As explained in the theory, the chain distribution changes as a function of oxidation reactions and alters the active chain concentrations $c(t)$. Following Eq. 12, let us consider the chain detachment happens as a function of ξ_3 , $f_d = k_d \xi_3$. Similarly, the chain reattachment happens as a function of ξ_6 as $f_a = k_a \xi_6$. For $k_d > k_a$ condition, the number of active chains decreases leading to a decrease in the shear modulus (G_{shear}) as seen in Fig. 7(a), (b) and (d). On the other hand, when $k_a > k_d$, we observe an increase in G_{shear} , as demonstrated in Fig. 7(c). The contour plots of the limiting stretchability parameter, λ_L

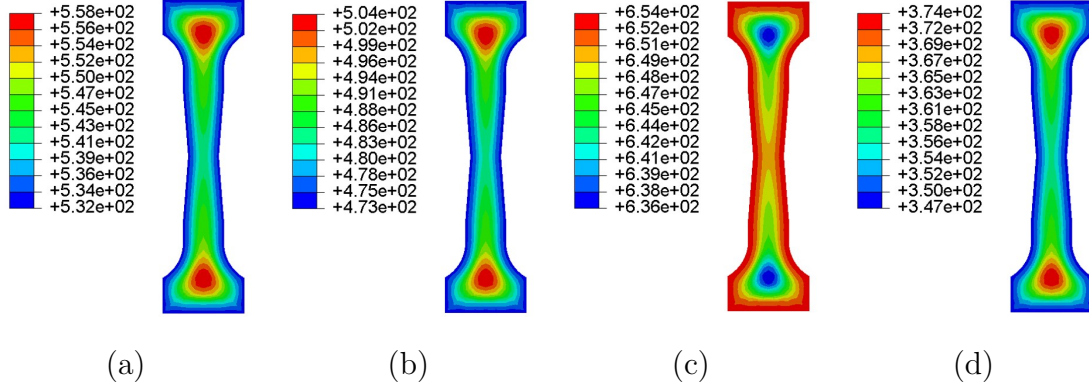


Figure 7: Contour plots of shear modulus after (a) 30 hours, (b) after 50 hours (with $k_a < k_d$), (c) 50 hours ($k_a > k_d$) and (d) 100 hours (in MPa).

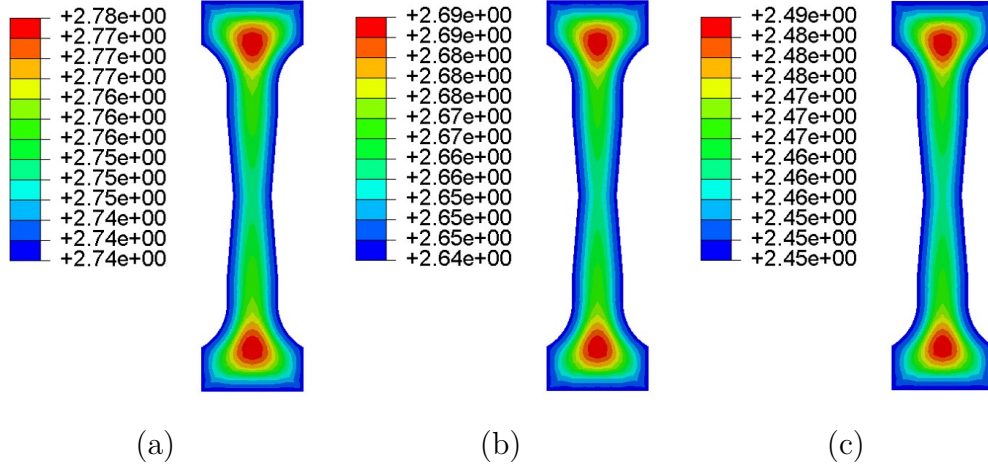


Figure 8: Contour plots of λ_L after (a) 30 hours, (b) 50 hours and (c) 100 hours (with $k_a < k_d$).

at various stages of oxidation are also shown in Fig. 8. It is important to note that λ_L is essentially a function of the dissociated chain ratio, c_{rd} . As the oxidation progresses, the number of dissociated chains goes up, leading to an increase in c_{rd} for the $k_a < k_d$ condition; which in turn causes a reduction in the stretchability, as shown in Fig. 8(a), (b) and (c).

The changes in the material properties further lead to a change in the constitutive response of the polymer. Fig. 9 shows the force versus displacement plots for the dogbone samples

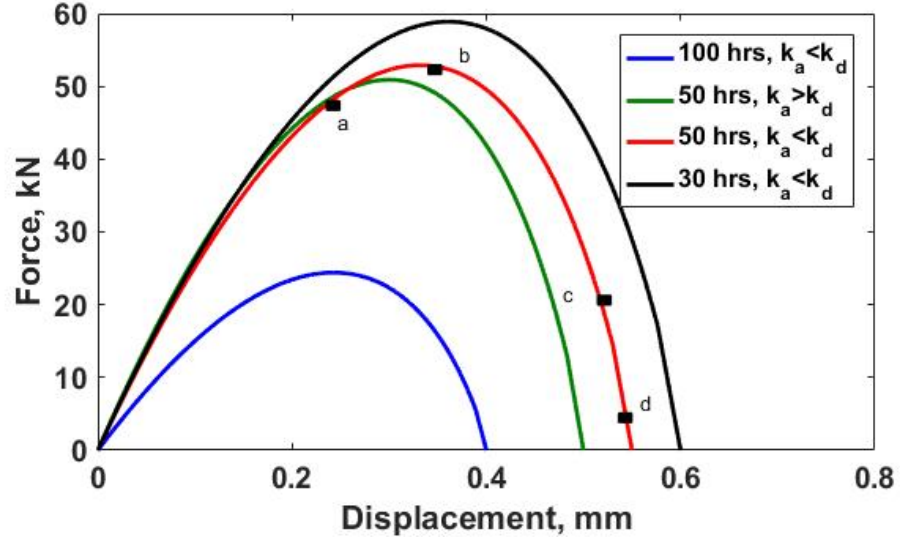


Figure 9: Force vs displacement plots for the dogbone samples subjected to tensile loading upon oxidation for various hours.

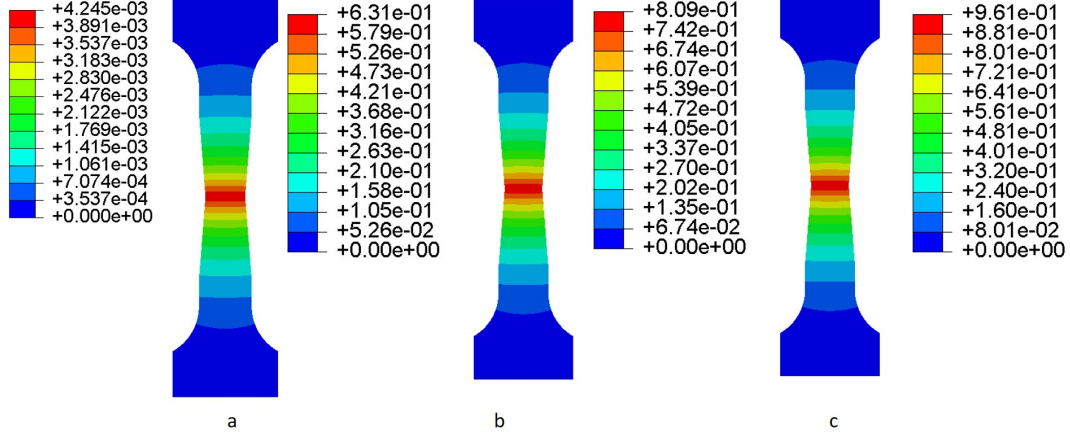


Figure 10: Contour plots of the phase field variable d at significant points in the force-displacement plot as marked a, b, c and d in Fig. 9.

oxidized for several hours. In general, a significant drop in the limiting stretchability and tensile strength has been observed due to oxidation. Approximately 18.33% drop in the failure

strain has been noticed after 100 hours of oxidation. The maximum tensile strength of the material also decreases significantly. We also observe a slight change in the stiffness of the material during the initial period of oxidation (between 30 to 50 hours), which significantly decreases upon further oxidation (at 100 hours). Fig. 10 shows the damage contours of the dogbone sample corresponding to the significant points in the load-deformation curve as denoted in Fig. 9 for 50 hours of oxidation (corresponding to $k_a < k_d$ condition). At point a, damage initiates with a very small value at ≈ 0.3 mm of displacement. The force continues to increase beyond this point until it reaches the peak at point b corresponding to a displacement of ≈ 0.4 mm. The respective contour of the phase field variable is shown in Fig. 10 b. The continued loading of the sample ultimately causes rupture of the material, as shown by c and d in Fig. 9 with corresponding damage contours in Fig. 10c and d, respectively.

Oxidation in the presence of mechanical loading (stress-coupled):- In order to identify the effect of external loading on the polymer sample simultaneously undergoing oxidation, we consider the same dogbone geometry as shown in Fig. 5(a). The displacement (mechanical) boundary condition as applied to simulate the stress-coupled situation is demonstrated in Fig. 11(a). We have applied a total displacement of 1 mm on the top surface of the sample in a ramp-like manner over the period of 2 hours and then hold it for a total of 50 hours. The chemical boundary condition remains the same as Fig. 5(b) for the 50hrs period. Hence the sample is allowed to oxidize for 50hrs under a constant displacement of 1mm. Fig. 11(b) shows the load vs. time plot for the simulation. A quantitative comparison between the stress-coupled situation and the two-step analysis (case 1) is not realistic as the boundary conditions are completely different. From Fig. 11(b), we see that the material behavior is dominated by the mechanical deformation for the first 2 hours. Subsequently, the response is predominantly driven by the oxidation process, as the displacement is held constant after 2 hrs. The material eventually fails as an effect of the degraded mechanical properties caused due to the network embrittlement during oxidation. Since the displacement is held constant at a value of 1 mm, we see the load starts to drop at the corresponding value until complete failure happens in Fig. 11(c).

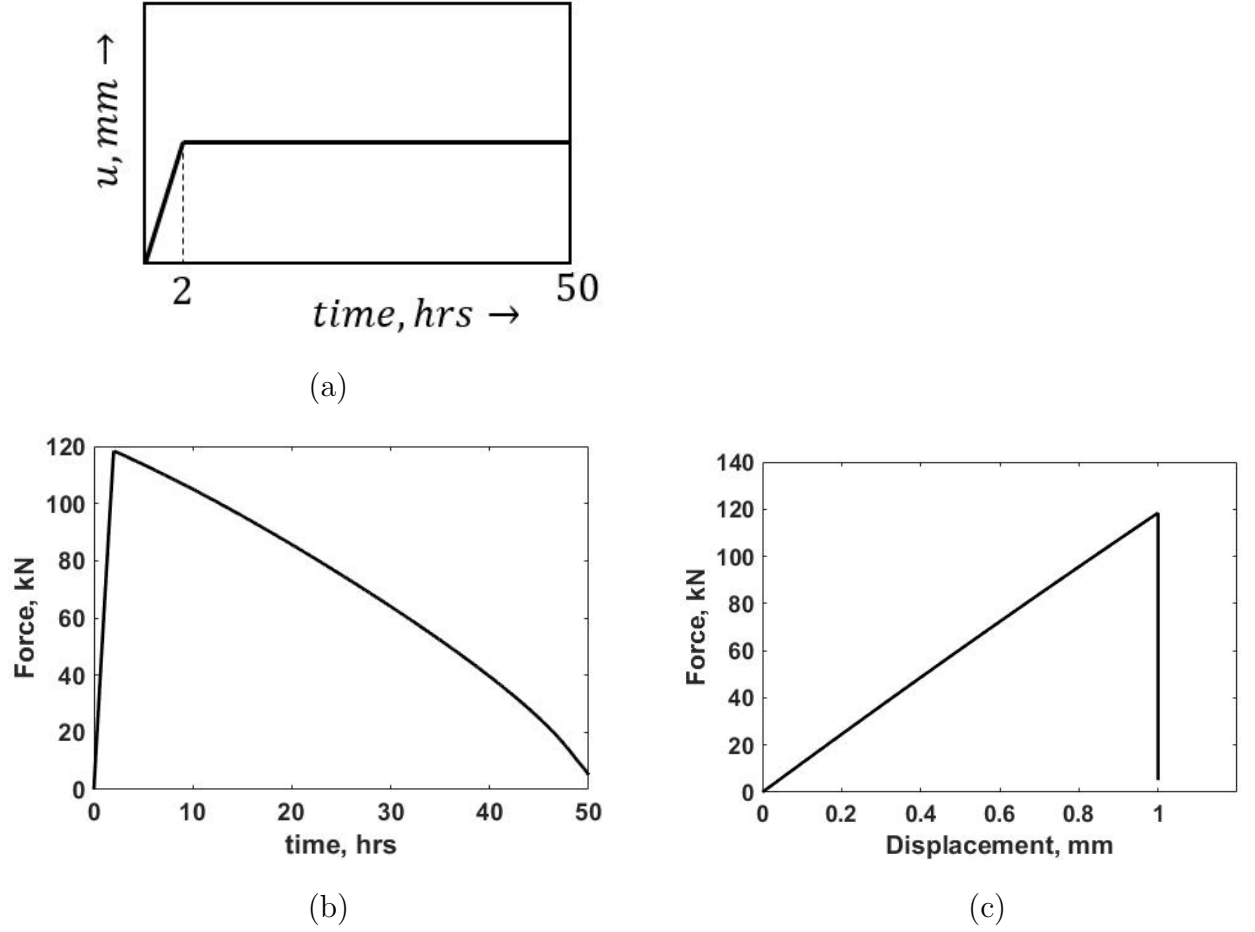


Figure 11: (a) Displacement boundary condition for the dogbone sample for a stress-coupled oxidation situation; (b) the force vs. time plot for a constant deformation+oxidation (stress coupled); (c) the corresponding force vs. displacement plot.

4.2. Case study-2: Oxidation followed by Mode-I loading on a single-edge-notched plate

In this example, we attempt to predict the response of a polymer specimen containing a pre-existing crack undergoing oxidation. In reality, the presence of cracks promotes oxygen diffusion providing favorable paths. Hence pre-existing flaws make the material more prone to oxidation near and around the crack-zones. To simulate one such scenario, we choose to study the effect of oxidation on a single-edge-notched polymer plate, as shown in Fig. 12a. As earlier, the kinetic and material parameters are chosen from Table B.1 and B.2, respectively.

The chemical boundary condition is considered as the same as in case study 1. In this simulation, we assume that, oxygen diffuses from the left side of the sample, and all other edges are impermeable. We let the sample to oxidize at 80°C for 100 hours. Following which, the oxidized sample is pulled at a rate of $1 \times 10^{-3}\text{mm/s}$ along the top-edge, till the final fracture occurs.

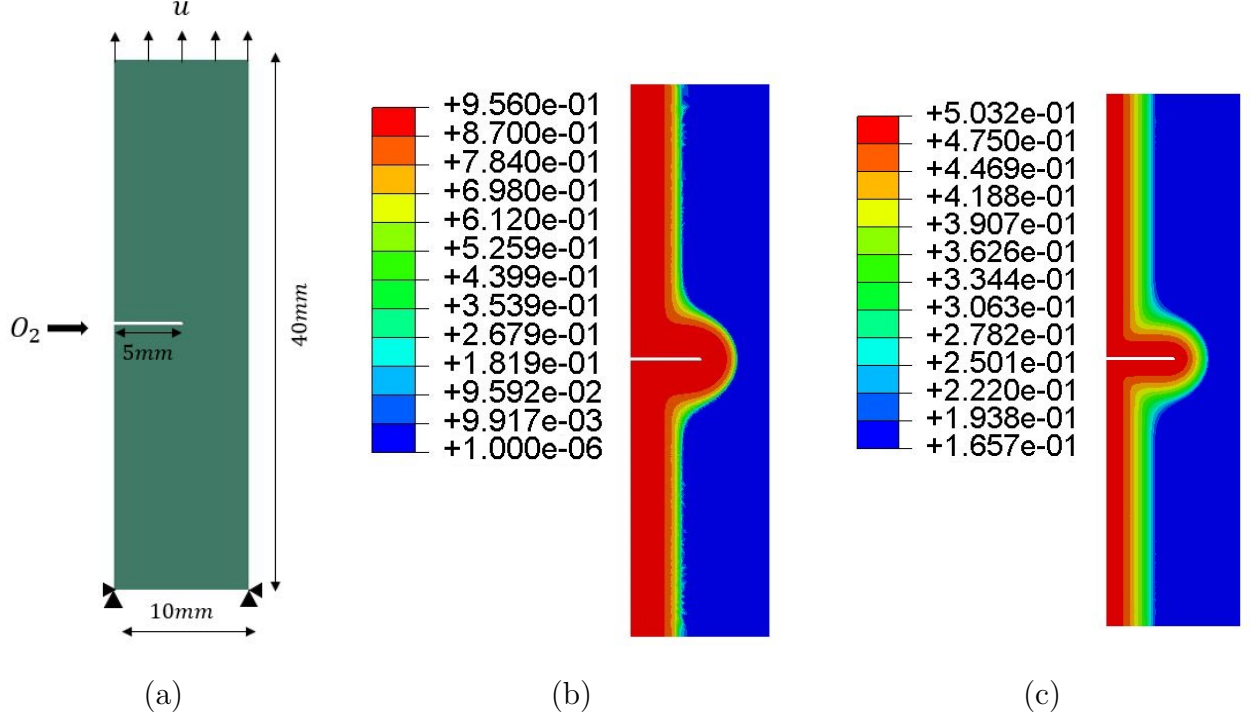


Figure 12: (a) Geometry of the single-edge-notched tension sample showing the displacement and diffusion boundary conditions; Contour plots of the (b) extent of reaction (III), ξ_3 showing resin depletion; (c) chain dissociation ratio c_{rd} after 100 hours of oxidation.

Fig. 12(b) and (c) show the contour plots of extent of reaction, ξ_3 and the chain dissociation ratio, c_{rd} , respectively after 100 hours of oxidation. As seen in Fig. 12(b), ξ_3 reaches to a value of 0.946 at the outermost surface along the left boundary as well as around the crack tip, indicating chain-scission would take place predominantly within this zone. As a result, the chain dissociation ratio continues to increase and reaches a value of $\approx 50\%$ on the left surface and around the crack tip after 100 hrs as shown in Fig. 12(c). This phe-

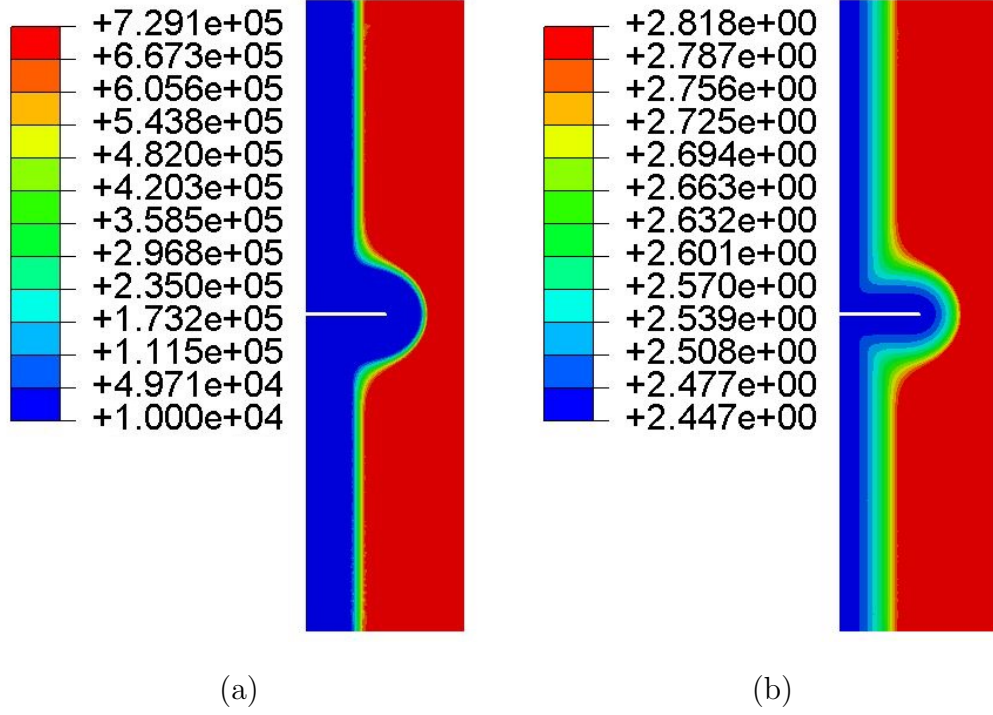


Figure 13: Contour plots of (a) G_c ; (b) λ_L after 100 hours of oxidation.

nomenon further leads to a reduction in the limiting chain extensibility and Griffith-type fracture energy in the oxidized zones, as shown in Fig. 13. The Griffith-type fracture energy drops significantly in the oxidized zone, from 1.44 kN/mm to 10 N/mm after 100 hrs of oxidation, as seen from Fig. 13(a). The limiting chain extensibility also drops down to 2.447 on the left surface compared to the unoxidized value of 3.0 for the virgin polymer as shown in Fig. 13(b). Consequently, these events affect the load-displacement response of the material as demonstrated in Fig. 14(a). After 100 hrs of oxidation, we see a significant drop in the maximum load, compared to the virgin material (as $\approx 62\%$). Similarly, the stretchability of the oxidized material has been dropped compared to the virgin material, as seen from the ultimate displacement values corresponding to final fracture. Fig. 14(b) shows the phase field contour plots of the oxidized polymer sample corresponding to the locations marked by a, b and c in the force-displacement curve. The sample reaches to the maximum load

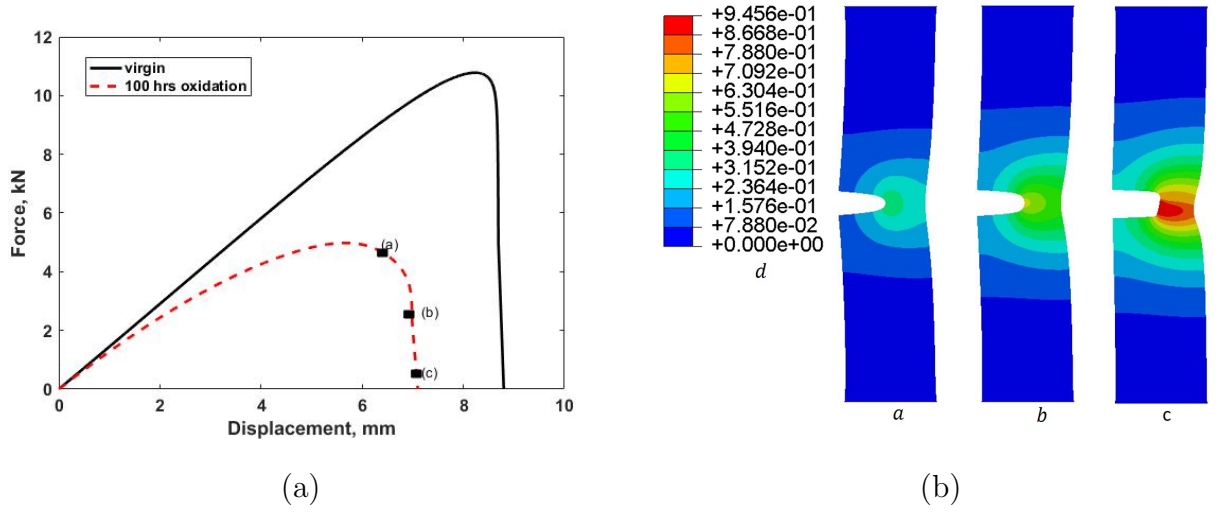


Figure 14: (a) Force vs. displacement plot of the single-edge-notch sample shown in Fig. 12(a) ; (b) Contour plots of the phase field variable d at significant points in the force-displacement plot marked as a, b, and c in Fig. 14(a) for the oxidized polymer.

just before the point a. Beyond this point, the load continues to drop with a continuous increase in the phase field parameter value. Finally the sample completely breaks at point c, with the maximum value of corresponding phase field parameter reaching 0.95, as shown in Fig. 14(b)-c.

5. Concluding remark

In this work, we have developed a reaction-driven evolving polymer network theory coupled with phase-field fracture to model the high temperature oxidative degradation and fracture in amorphous polymers. The proposed theory considers the closed-loop chain reaction kinetics occurring at the polymer chain level and successfully incorporates them into the statistical mechanics based network theory to account for the network alternation and mechanical property degradation. The proposed theory is capable of quantifying and reflecting the network level changes (degradation) in the polymer via the active and dissociated chain ratios; both of which evolve as a function of oxidative crosslinking and chain scission. Upon establishing a seamless connection between the micro and macro-scale kinematics the

continuum level constitutive response of the material is further derived. In addition, we have used a continuum level phase-field fracture theory to model the macroscopic damage and fracture originating due to the prolonged oxidation in the material. We further tested the capability of the proposed model by numerically implementing it in a commercial FE-setting and performing several important case studies. It is observed that the proposed model is capable of predicting the embrittlement of the materials caused by the high-temperature oxidative aging, and macroscopic damage propagation and fracture. In the future, we plan to extend the proposed model to capture the effect of oxidation-induced embrittlement in the anisotropic deformation setting in polymer matrix composites (PMC) and perform experimental validation.

6. Acknowledgment

The authors would like to acknowledge the super-computing resources from the SUPERIOR computing facility at MTU.

Appendix A. Evolution of the chain distribution tensor

- while no oxidation (or chemical reaction is taking place), pure deformation Eq. 25 can be concisely written as,

$$\dot{\boldsymbol{\mu}} = \mathbf{D}\boldsymbol{\mu} + \boldsymbol{\mu}\mathbf{D} \quad (\text{A.1})$$

with all other reaction-dependent terms being zero and assuming the un-reacted network as incompressible. In such case, the solution for $\boldsymbol{\mu}$ turns out to be $\boldsymbol{\mu} = \mathbf{F}\mathbf{F}^T$, which is equivalent to the left Cauchy-Green strain tensor as, $\mathbf{B} = \mathbf{F}\mathbf{F}^T$. [88].

- when the mechanical deformation is held constant ($\mathbf{F} = \mathbf{I}$) and oxidation (only chemical reactions) is allowed to happen

Introducing,

$$\alpha = (\xi_4 + \xi_5 + \xi_6) \frac{C_T - c(t)}{c(t)} \quad (\text{A.2})$$

and $\beta = \xi_{1a} + \xi_{1b} + \xi_3$ in Eq. 25, we get,

$$\dot{\boldsymbol{\mu}} = k_a \alpha \mathbf{I} - \left[k_d \beta + \frac{\dot{c}(t)}{c(t)} \right] \boldsymbol{\mu} + (\boldsymbol{\mu} + \boldsymbol{\mu}^T) \quad (\text{A.3})$$

Following which, the solution of $\boldsymbol{\mu}$ turns out as,

$$\boldsymbol{\mu} = \mathbf{F} e^{-(k_d \beta + c_m)t} \mathbf{F}^T + \frac{k_a \alpha}{k_d \beta + c_m} \mathbf{F} \mathbf{F}^T \quad (\text{A.4})$$

where $c_m = \frac{\dot{c}(t)}{c(t)}$, is used.

Appendix B. Parameters used in the numerical simulation

K_{bulk}	5 GPa ([54])
ν	0.45 ([54])
G_0	0.58GPa ([54])
$G_{c,un}$	1.44 kN/mm
$G_{c,ox}$	10 N/mm
$\lambda_L(un)$	3
$\lambda_L(ox)$	1.9
$c_{rd,ox}$	≈ 1.0
$c(t_0)$	$0.58e9 \text{ mol}/m^3$
$C_T(t_0)$	$0.7e9 \text{ mol}/m^3$

Table B.1: Material parameters for a representative elastomer undergoing oxidation

Table B.2: Kinetic parameters related to diffusion and reaction kinetics for a typical polymer undergoing oxidation ([52])

Parameter	Unit	Value	Reference
Solubility coefficient, S	$mol - L^{-1} Pa^{-1}$	1.4×10^{-8}	[73]
Diffusivity, D	$m^2 s^{-1}$	8.8×10^{-5}	[72]
Diffusive activation energy, E_d	kJ/mol	36.5	[73]
Reaction rate constants			
k_2	$1/MPa - s$	2.84×10^{-9}	calibrated
k_3	$1/MPa - s$	2.9×10^{-9}	calibrated
k_6	$1/MPa - s$	2.76×10^{-9}	calibrated
Q_2	kJ/mol	30	[73]
Q_3	kJ/mol	45	[73]
Q_6	kJ/mol	10	[73]
H_2	J/mol	128×10^6	[18]
H_3	J/mol	40.52×10^6	[18]
H_6	J/mol	267.26×10^6	[18]
Gas constant, R	$J/(mol \cdot K)$	8.31446	
χ		0.1	[24]
μ_0 at STP	J/mol	3.88×10^5	[44]
$c_0^{(PH)}$	mol/L	20	[72]
$c_0^{(POOH)}$	mol/L	1×10^{-4}	[72]

References

- [1] Abaqus, V., . 6.14. 2 user's manual.(2014). Dassault Systèmes Simulia Corp., Providence, RI, USA .
- [2] Ambati, M., Gerasimov, T., De Lorenzis, L., 2015. A review on phase-field models of brittle fracture and a new fast hybrid formulation. *Computational Mechanics* 55, 383–405.
- [3] Ames, N.M., Srivastava, V., Chester, S.A., Anand, L., 2009. A thermo-mechanically coupled theory for large deformations of amorphous polymers. part ii: Applications. *International Journal of Plasticity* 25, 1495–1539.
- [4] Anand, L., Ames, N.M., Srivastava, V., Chester, S.A., 2009. A thermo-mechanically coupled theory for large deformations of amorphous polymers. part i: Formulation. *International Journal of Plasticity* 25, 1474–1494.
- [5] Anand, L., Gurtin, M.E., 2003. A theory of amorphous solids undergoing large deformations, with application to polymeric glasses. *International Journal of Solids and Structures* 40, 1465–1487.
- [6] Anand, L., Mao, Y., Talamini, B., 2019. On modeling fracture of ferritic steels due to hydrogen embrittlement. *Journal of the Mechanics and Physics of Solids* 122, 280–314.
- [7] Arruda, E.M., Boyce, M.C., 1993a. Evolution of plastic anisotropy in amorphous polymers during finite straining. *International Journal of Plasticity* 9, 697–720.
- [8] Arruda, E.M., Boyce, M.C., 1993b. A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials .
- [9] Audouin, L., 2000. Kinetic modeling of low-temperature oxidation of hydrocarbon polymers. *Handbook of polymer degradation* , 727–763.

- [10] Audouin, L., Gueguen, V., Tcharkhtchi, A., Verdu, J., 1995. “close loop” mechanistic schemes for hydrocarbon polymer oxidation. *Journal of Polymer Science Part A: Polymer Chemistry* 33, 921–927.
- [11] Audouin, L., Langlois, V., Verdu, J., De Bruijn, J., 1994. Role of oxygen diffusion in polymer ageing: kinetic and mechanical aspects. *Journal of Materials science* 29, 569–583.
- [12] Böger, L., Nateghi, A., Miehe, C., 2017. A minimization principle for deformation-diffusion processes in polymeric hydrogels: Constitutive modeling and fe implementation. *International Journal of Solids and Structures* 121, 257–274.
- [13] Bourdin, B., 2007. Numerical implementation of the variational formulation for quasi-static brittle fracture. *Interfaces and free boundaries* 9, 411–430.
- [14] Bourdin, B., Francfort, G.A., Marigo, J.J., 2000. Numerical experiments in revisited brittle fracture. *Journal of the Mechanics and Physics of Solids* 48, 797–826.
- [15] Bourdin, B., Francfort, G.A., Marigo, J.J., 2008. The variational approach to fracture. *Journal of elasticity* 91, 5–148.
- [16] Bowles, K.J., Nowak, G., 1988. Thermo-oxidative stability studies of celion 6000/pmr-15 unidirectional composites, pmr-15, and celion 6000 fiber. *Journal of Composite Materials* 22, 966–985.
- [17] Buliga, M., 1998. Energy minimizing brittle crack propagation. *Journal of Elasticity* 52, 201.
- [18] Calvert, J.G., Pitts, J.N., 1966. *Photochemistry* .
- [19] Celina, M., Gillen, K.T., Assink, R., 2005. Accelerated aging and lifetime prediction: review of non-arrhenius behaviour due to two competing processes. *Polymer Degradation and stability* 90, 395–404.

- [20] Celina, M., Wise, J., Ottesen, D., Gillen, K., Clough, R., 2000. Correlation of chemical and mechanical property changes during oxidative degradation of neoprene. *Polymer degradation and Stability* 68, 171–184.
- [21] Celina, M.C., 2013. Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polymer Degradation and Stability* 98, 2419–2429.
- [22] Chester, S.A., Anand, L., 2010. A coupled theory of fluid permeation and large deformations for elastomeric materials. *Journal of the Mechanics and Physics of Solids* 58, 1879–1906.
- [23] Chester, S.A., Anand, L., 2011. A thermo-mechanically coupled theory for fluid permeation in elastomeric materials: application to thermally responsive gels. *Journal of the Mechanics and Physics of Solids* 59, 1978–2006.
- [24] Chester, S.A., Di Leo, C.V., Anand, L., 2015. A finite element implementation of a coupled diffusion-deformation theory for elastomeric gels. *International Journal of Solids and Structures* 52, 1–18.
- [25] Colin, X., Audouin, L., Verdu, J., 2004. Determination of thermal oxidation rate constants by an inverse method. application to polyethylene. *Polymer Degradation and Stability* 86, 309–321.
- [26] Colin, X., Marais, C., Verdu, J., 2001a. A new method for predicting the thermal oxidation of thermoset matrices: application to an amine crosslinked epoxy. *Polymer Testing* 20, 795–803.
- [27] Colin, X., Marais, C., Verdu, J., 2001b. Thermal oxidation kinetics for a poly (bis-maleimide). *Journal of Applied Polymer Science* 82, 3418–3430.
- [28] Colin, X., Marais, C., Verdu, J., 2002. Kinetic modelling and simulation of gravimetric curves: application to the oxidation of bismaleimide and epoxy resins. *Polymer Degradation and Stability* 78, 545–553.

- [29] Colin, X., Verdu, J., 2003. Thermal ageing and lifetime prediction for organic matrix composites. *Plastics, rubber and composites* 32, 349–356.
- [30] Colin, X., Verdu, J., 2005. Strategy for studying thermal oxidation of organic matrix composites. *Composites Science and technology* 65, 411–419.
- [31] Colin, X., Verdu, J., 2012. Mechanisms and kinetics of organic matrix thermal oxidation, in: *Long-term durability of polymeric matrix composites*. Springer, pp. 311–344.
- [32] Dal Maso, G., Toader, R., 2002. A model for the quasi-static growth of brittle fractures: Existence and approximation results. *Archive for Rational Mechanics and Analysis* 162, 101–135.
- [33] Decelle, J., Huet, N., Bellenger, V., 2003. Oxidation induced shrinkage for thermally aged epoxy networks. *Polymer Degradation and Stability* 81, 239–248.
- [34] Drozdov, A., 1999. A constitutive model in finite thermoviscoelasticity based on the concept of transient networks. *Acta mechanica* 133, 13–37.
- [35] Ernault, E., Richaud, E., Fayolle, B., 2016. Thermal oxidation of epoxies: influence of diamine hardener. *Polymer Degradation and Stability* 134, 76–86.
- [36] Ernault, E., Richaud, E., Fayolle, B., 2017a. Origin of epoxies embrittlement during oxidative ageing. *Polymer Testing* 63, 448–454.
- [37] Ernault, E., Richaud, E., Fayolle, B., 2017b. Thermal-oxidation of epoxy/amine followed by glass transition temperature changes. *Polymer Degradation and Stability* 138, 82–90.
- [38] Fayolle, B., Audouin, L., Verdu, J., 2004. A critical molar mass separating the ductile and brittle regimes as revealed by thermal oxidation in polypropylene. *Polymer* 45, 4323–4330.
- [39] Fayolle, B., Colin, X., Audouin, L., Verdu, J., 2007. Mechanism of degradation induced embrittlement in polyethylene. *Polymer Degradation and Stability* 92, 231–238.

- [40] Fayolle, B., Richaud, E., Verdu, J., Farcas, F., 2008. Embrittlement of polypropylene fibre during thermal oxidation. *Journal of materials science* 43, 1026–1032.
- [41] Flory, P., 1953. *Principles of polymer chemistry*; cornell university. Ithaca, New York 579.
- [42] Francfort, G.A., Marigo, J.J., 1998. Revisiting brittle fracture as an energy minimization problem. *Journal of the Mechanics and Physics of Solids* 46, 1319–1342.
- [43] Gent, A.N., 1996. A new constitutive relation for rubber. *Rubber chemistry and technology* 69, 59–61.
- [44] Gibbs, J.W., 1902. *Elementary principles in statistical mechanics: developed with especial reference to the rational foundation of thermodynamics*. C. Scribner’s sons.
- [45] Gigliotti, M., Minervino, M., Lafarie-Frenot, M., 2016a. Thermo-oxidative induced shrinkage in organic matrix composites for high temperature applications: effect of fibre arrangement and oxygen pressure. *Composite Structures* 146, 176–186.
- [46] Gigliotti, M., Minervino, M., Lafarie-Frenot, M., Grandidier, J., 2016b. Effect of thermo-oxidation on the local mechanical behaviour of epoxy polymer materials for high temperature applications. *Mechanics of Materials* 101, 118–135.
- [47] Gigliotti, M., Olivier, L., Vu, D.Q., Grandidier, J.C., Lafarie-Frenot, M.C., 2011. Local shrinkage and stress induced by thermo-oxidation in composite materials at high temperatures. *Journal of the Mechanics and Physics of Solids* 59, 696–712.
- [48] Govaert, L., Timmermans, P., Brekelmans, W., 2000. The influence of intrinsic strain softening on strain localization in polycarbonate: modeling and experimental validation. *Journal of Engineering Materials and Technology* 122, 177–185.
- [49] Gurtin, M.E., Fried, E., Anand, L., 2010. *The mechanics and thermodynamics of continua*. Cambridge University Press.

- [50] Holzapfel, A.G., 2000. Nonlinear solid mechanics ii .
- [51] Horgan, C.O., Saccomandi, G., 2002. A molecular-statistical basis for the gent constitutive model of rubber elasticity. *Journal of Elasticity* 68, 167–176.
- [52] Konica, S., Sain, T., 2020. A thermodynamically consistent chemo-mechanically coupled large deformation model for polymer oxidation. *Journal of the Mechanics and Physics of Solids* 137, 103858.
- [53] Kuhn, W., Gr $\ddot{u}$ n, F., 1946. Statistical behavior of the single chain molecule and its relation to the statistical behavior of assemblies consisting of many chain molecules. *Journal of polymer science* 1, 183–199.
- [54] KUMAR, M., GAUR, K.K., SHAKHER, C., 2015. Measurement of material constants (young’s modulus and poisson’s ratio) of polypropylene using digital speckle pattern interferometry (dsp). *Journal of the Japanese Society for Experimental Mechanics* 15, s87–s91.
- [55] Leibler, L., Sekimoto, K., 1993. On the sorption of gases and liquids in glassy polymers. *Macromolecules* 26, 6937–6939.
- [56] Loeffel, K., Anand, L., 2011. A chemo-thermo-mechanically coupled theory for elastic–viscoplastic deformation, diffusion, and volumetric swelling due to a chemical reaction. *International Journal of Plasticity* 27, 1409–1431.
- [57] Long, R., Qi, H.J., Dunn, M.L., 2013. Modeling the mechanics of covalently adaptable polymer networks with temperature-dependent bond exchange reactions. *Soft Matter* 9, 4083–4096.
- [58] Mao, Y., Anand, L., 2018. A theory for fracture of polymeric gels. *Journal of the Mechanics and Physics of Solids* 115, 30–53.
- [59] Mao, Y., Talamini, B., Anand, L., 2017. Rupture of polymers by chain scission. *Extreme Mechanics Letters* 13, 17–24.

- [60] Martínez-Pañeda, E., Golahmar, A., Niordson, C.F., 2018. A phase field formulation for hydrogen assisted cracking. *Computer Methods in Applied Mechanics and Engineering* 342, 742–761.
- [61] Miehe, C., Hofacker, M., Welschinger, F., 2010a. A phase field model for rate-independent crack propagation: Robust algorithmic implementation based on operator splits. *Computer Methods in Applied Mechanics and Engineering* 199, 2765–2778.
- [62] Miehe, C., Schaezel, L.M., Ulmer, H., 2015. Phase field modeling of fracture in multi-physics problems. part i. balance of crack surface and failure criteria for brittle crack propagation in thermo-elastic solids. *Computer Methods in Applied Mechanics and Engineering* 294, 449–485.
- [63] Miehe, C., Welschinger, F., Hofacker, M., 2010b. Thermodynamically consistent phase-field models of fracture: Variational principles and multi-field fe implementations. *International Journal for Numerical Methods in Engineering* 83, 1273–1311.
- [64] Minervino, M., Gigliotti, M., Lafarie-Frenot, M., Grandidier, J., 2013. The effect of thermo-oxidation on the mechanical behaviour of polymer epoxy materials. *Polymer Testing* 32, 1020–1028.
- [65] Minervino, M., Gigliotti, M., Lafarie-Frenot, M., Grandidier, J., 2014. A coupled experimental/numerical approach for the modelling of the local mechanical behaviour of epoxy polymer materials. *Journal of the Mechanics and Physics of Solids* 67, 129–151.
- [66] Mohammadi, H., Morovati, V., Poshtan, E., Dargazany, R., 2020. Understanding decay functions and their contribution in modeling of thermal-induced aging of cross-linked polymers. *Polymer Degradation and Stability* , 109108.
- [67] Narayan, S., Anand, L., 2019. A gradient-damage theory for fracture of quasi-brittle materials. *Journal of the Mechanics and Physics of Solids* 129, 119–146.

- [68] Olivier, L., Ho, N., Grandidier, J., Lafarie-Frenot, M., 2008. Characterization by ultra-micro indentation of an oxidized epoxy polymer: correlation with the predictions of a kinetic model of oxidation. *Polymer Degradation and Stability* 93, 489–497.
- [69] Pecora, M., Pannier, Y., Lafarie-Frenot, M.C., Gigliotti, M., Guigon, C., 2016. Effect of thermo-oxidation on the failure properties of an epoxy resin. *Polymer Testing* 52, 209–217.
- [70] Pochiraju, K., Tandon, G., Schoeppner, G., 2008. Evolution of stress and deformations in high-temperature polymer matrix composites during thermo-oxidative aging. *Mechanics of Time-Dependent Materials* 12, 45–68.
- [71] Quintana, A., Celina, M.C., 2018. Overview of dlo modeling and approaches to predict heterogeneous oxidative polymer degradation. *Polymer Degradation and Stability* 149, 173–191.
- [72] Richaud, E., Farcas, F., Bartolomé, P., Fayolle, B., Audouin, L., Verdu, J., 2006. Effect of oxygen pressure on the oxidation kinetics of unstabilised polypropylene. *Polymer Degradation and Stability* 91, 398–405.
- [73] Rincon-Rubio, L., Fayolle, B., Audouin, L., Verdu, J., 2001. A general solution of the closed-loop kinetic scheme for the thermal oxidation of polypropylene. *Polymer Degradation and Stability* 74, 177–188.
- [74] Rubinstein, M., Colby, R.H., et al., 2003. *Polymer physics*. volume 23. Oxford university press New York.
- [75] Sain, T., Loeffel, K., Chester, S., 2018. A thermo-chemo-mechanically coupled constitutive model for curing of glassy polymers. *Journal of the Mechanics and Physics of Solids* 116, 267–289.
- [76] Schoeppner, G., Tandon, G., Ripberger, E., 2007. Anisotropic oxidation and weight

- loss in pmr-15 composites. *Composites Part A: Applied Science and Manufacturing* 38, 890–904.
- [77] Scholes, C.A., Stevens, G.W., Kentish, S.E., 2010. The effect of hydrogen sulfide, carbon monoxide and water on the performance of a pdms membrane in carbon dioxide/nitrogen separation. *Journal of Membrane Science* 350, 189–199.
 - [78] Strobl, G.R., Strobl, G.R., 1997. *The physics of polymers. volume 2.* Springer.
 - [79] Talamini, B., Mao, Y., Anand, L., 2018. Progressive damage and rupture in polymers. *Journal of the Mechanics and Physics of Solids* 111, 434–457.
 - [80] Tanaka, F., Edwards, S., 1992. Viscoelastic properties of physically crosslinked networks. 1. transient network theory. *Macromolecules* 25, 1516–1523.
 - [81] Tandon, G., Pochiraju, K., Schoeppner, G., 2006. Modeling of oxidative development in pmr-15 resin. *Polymer Degradation and Stability* 91, 1861–1869.
 - [82] Tandon, G., Pochiraju, K., Schoeppner, G., 2008. Thermo-oxidative behavior of high-temperature pmr-15 resin and composites. *Materials Science and Engineering: A* 498, 150–161.
 - [83] Treolar, L., 1975. *The physics of rubber elasticity.* clarendon.
 - [84] Ulm, F.J., Coussy, O., Kefei, L., Larive, C., 2000. Thermo-chemo-mechanics of asr expansion in concrete structures. *Journal of engineering mechanics* 126, 233–242.
 - [85] Veitmann, M., Jumeau, R., Bourson, P., Ferriol, M., Lahure, F., 2014. Understanding and control of high temperature oxidation flaws of low-density poly(ethylene) with raman spectroscopy. *International Journal of Spectroscopy* 2014, 1–9. doi:10.1155/2014/194563.
 - [86] Vernerey, F.J., 2018. Transient response of nonlinear polymer networks: A kinetic theory. *Journal of the Mechanics and Physics of Solids* 115, 230–247.

- [87] Vernerey, F.J., Brighenti, R., Long, R., Shen, T., 2018. Statistical damage mechanics of polymer networks. *Macromolecules* 51, 6609–6622.
- [88] Vernerey, F.J., Long, R., Brighenti, R., 2017. A statistically-based continuum theory for polymers with transient networks. *Journal of the Mechanics and Physics of Solids* 107, 1–20.
- [89] Wise, J., Gillen, K., Clough, R., 1997. Quantitative model for the time development of diffusion-limited oxidation profiles. *Polymer* 38, 1929–1944.
- [90] Wu, P., Van Der Giessen, E., 1993. On improved network models for rubber elasticity and their applications to orientation hardening in glassy polymers. *Journal of the Mechanics and Physics of Solids* 41, 427–456.
- [91] Yeh, C.J., Dowland, M., Schmidt, R.G., Shull, K.R., 2016. Fracture and thermal aging of resin-filled silicone elastomers. *Journal of Polymer Science Part B: Polymer Physics* 54, 263–273.