Physics-based Constitutive Equation for Thermo-Chemically Aged Elastomers based on Crosslink Density Evolution

Maryam Shakiba[1,2]*, Aimane Najmeddine[1]

[1]*Department Civil and Environmental Engineering, Virginia Tech, USA*

[2]*Macromolecules Innovation Institute (MII), Virginia Tech, USA*

Abstract

This paper presents a physics-based constitutive equation to predict the mechanical responses of thermo-chemically aged elastomers. High-temperature oxidation in elastomers is a complex phenomenon. The macromolecular network of elastomers' microstructures undergoes chain scission and crosslinking under high temperature and oxygen saturation conditions. In this work, we modify the network stiffness and the chain extensibility in the well-known Arruda-Boyce constitutive equation to incorporate network changes in the microstructures of elastomers during thermo-chemical aging. In particular, the effects of network evolution due to aging in changing the shear modulus and the number of Kuhn monomers are considered. The modification is based on chemical characterization tests measuring the crosslink density evolution. The developed constitutive equation predicts the mechanical responses of thermo-chemically aged elastomers independently of any mechanical tests on aged samples. The proposed constitutive equation is validated with respect to a comprehensive set of experimental data available in the literature that were designed to capture thermo-chemical aging effects in elastomers. The comparison showed that the developed constitutive equation can accurately predict the tensile tests conducted on aged samples based on crosslink density evolution input. The obtained constitutive equation is physics-based, simple, and includes minimal material parameters.

---

*Corresponding author.
Email address: `mshakiba@vt.edu` (Maryam Shakiba[1,2])

Preprint submitted to International Journal of Solids and Structures *February 19, 2022*

Keywords: Thermo-chemical aging, Crosslink density, Large deformation, Elastomer aging, Oxidation

---

1. Introduction

Elastomers are widely used in a variety of engineering applications such as medical devices, aerospace components, and civil infrastructure thanks to their exceptional mechanical and chemical properties. Under operation, elastomers often experience mechanical loading and are exposed to oxygen and elevated temperatures. Thermo-chemical aging due to oxygen diffusion or thermal stresses is an irreversible mechanism that degrades the mechanical properties of elastomers and compromises their desired long-term performance (Hutchinson, 1995). Therefore, the durability of elastomers strongly depends on how thermo-chemical aging affects their mechanical properties. Hence, understanding and predicting the mechanical responses of thermo-chemically aged elastomers play a crucial role in product development.

The mechanical behavior of elastomers is intrinsically complicated. Thermo-chemical aging in elastomers itself is a complex multiphysics phenomenon that makes the characterization of elastomers all the more challenging. Understanding the behavior of thermo-chemically aged elastomers is difficult due to the fact that the aging process is slow, several changes in the macromolecular network are at work, and deformations are large. In the following, the studies on the characterization of thermo-chemical aging in elastomers and the developed continuum mechanics approaches to predict the mechanical responses of aged elastomers are presented.

1.1. Literature review of the characterization of thermo-chemical aging mechanism

Thermo-chemical aging in elastomers due to high-temperature conditions and oxygen diffusion causes chemical reactions which lead to chain scission, crosslink breakage, and crosslink formation (e.g., Tobolsky et al. (1944); Blum et al. (1951); Gillen et al. (1995)). Celina (2013) presented a comprehensive review on the approaches for predicting elastomers thermo-chemical aging. Chain-scission reactions break the chains and cause degradation of the original network. Meanwhile, more crosslinks form between the original polymer chains as well as the newly formed chains due to chain-scission. Therefore, thermo-chemical aging can be described by two competing mechanisms, network degradation and network reformation process (e.g., Achenbach & Duarte (2003); Wineman (2009); Mohammadi et al. (2020); Beurle et al. (2020)). The relative rate of chain-scission and crosslink formation is essentially what determines whether the material becomes more ductile or more brittle. Although it must be noted that even if the thermo-chemical kinetics of the chain-scission and crosslinking reactions are similar, the aged material would not have the same toughness like that of the virgin material due to changes in the length of polymer chains (Mohammadi et al., 2020).

The literature agrees that most polymer chains tend to crosslink under oxidative conditions, leading to an increase in the modulus and the hardening with embrittlement (Wise et al., 1995, 1997a,b; Celina et al., 1998, 2000a,b; Celina, 2013). Hamed & Zhao (1999) performed a series of swelling measurements on Styrene-Butadiene Rubber (SBR) and Natural Rubber (NR) and showed that immediately after an initial aging period, these elastomers exhibit an increase in the crosslink density. The authors concluded that after an initial aging duration where network chain formation and disruption events are similar, the network formation occurs in greater amounts compared to the disruption when aging time is further increased. Shaw et al. (2005) and Johlitz et al. (2014) observed that the increase in the elastomer stiffness is more pronounced than the network degradation under thermo-chemical aging. Tensile tests conducted on several aged specimens showed an increase in the stiffness even under low temperatures and short aging times. However, the difference in the relaxation test data (i.e., tests where stretched specimens are being aged and the stress is continuously measured) was less at lower temperatures. Thus, the authors concluded that network reformation is more dominant in thermo-chemical aging of elastomers.

Similarly, Rezig et al. (2020) conducted several mechanical experiments on aged SBR for different temperatures and exposure times. They observed higher stiffness at higher temperatures (temperatures up to 100°C) and at longer exposure times and concluded that such behavior is indicative of a crosslinking process as the predominant mechanism of thermo-chemical aging for SBR material. Moreover, based on a few chemical characterization tests, Zhi et al. (2019) investigated the elastomer's chain network during aging and showed that chain-scission reactions remain nearly unchanged in the initial aging stage; however, as aging time increases, more dangling chain ends are formed and crosslink density increases. Finally, Konica & Sain (2021) stated that an oxidized product has a more crosslinked network of smaller chains compared to the unaged polymer with the longer crosslinked network.

1.2. Literature review of developed thermo-chemical aging constitutive equations

During the last few decades, several researchers modeled multi-physics aging of elastomers and polymers including chemical reactions, diffusion, and mechanical coupling (e.g., Achenbach & Duarte (2003); Shaw et al. (2005); Pochiraju & Tandon (2006); Gigliotti et al. (2011); Steinke et al. (2011); Johlitz et al. (2011); Johlitz & Lion (2013); Johlitz et al. (2014); Shakiba et al. (2014, 2016); Lejeunes et al. (2018); Konica & Sain (2020)). Phenomenological and thermodynamic-based frameworks were developed to combine diffusion and reaction expressions to link mechanical responses to chemical kinetics (e.g., Wise et al. (1997a,b); Pochiraju & Tandon (2006)). Johlitz et al. (Lion & Johlitz, 2012; Johlitz et al., 2014; Johlitz & Lion, 2013) formulated a constitutive approach by evaluating the Clausius-Planck inequality and continuum damage mechanics. They employed the concept of state variables to describe the scission reactions of the primary network and the crosslink reactions creating the secondary network. Wineman & Shaw (2019) developed a constitutive theory for elastomers at elevated temperatures representing the chemical kinetics of scission, re-coiling, and re-crosslinking, that were expressed in terms of activation energies. Other researchers assumed a temporal evolution of the material properties to incorporate the variation in stiffness upon subjecting the elastomer to different multi-physics phenomena like curing or thermo-oxidative aging (Dal & Kaliske, 2009; Hossain & Steinmann, 2015).

Moreover, micro-mechanical constitutive equations based on statistical mechanics of polymer structure were developed (e.g., Mohammadi et al. (2020); Beurle et al. (2020); Konica & Sain (2021)). Mohammadi et al. (2020) developed a micro-mechanical model based on the competition between chain-scission and crosslinking events occurring at the polymer network during oxidation. Konica & Sain (2021) developed an oxidation reaction-informed evolving network theory to connect the microscale network evolution with macroscopic damage occurring in polymers. They used the transient network theory based on the statistical mechanics framework of the polymer chains to model the microscale network evolution yielded by the chemical reactions. Zhi et al. (2019) established a hyper-viscoelastic constitutive equation according to the alteration of the macromolecular network observed in experiments to capture the mechanical behavior of SBR at different aging states.

In summary, the developed constitutive equations have either assumed the form of thermodynamic energies phenomenologically, been dependent on the types of mechanical tests, or provided no robust link of the changes in the elastomers' macromolecular network to chemical pathways. Some of the more complicated frameworks are essentially mechanical theories and have yet to be verified fully experimentally. Moreover, the more recently developed constitutive equations in the literature despite making great progress rely on several either mechanical tests or chemistry kinetics characterizations to obtain numerous model parameters. Thus, although much work has been accomplished in the experimental and the simulation aspects, a practical link between the network evolution and the mechanical responses in aged elastomers' is still missing.

1.3. Objectives and summary

This paper develops a physics-based constitutive equation to predict the mechanical response of thermo-chemically aged elastomers based on their chemical macromolecular changes. The main contribution is to connect the form of free energy directly to chemical characterization experiments. The Helmholtz free energy is modified to include the effects of macromolecular network evolution upon aging. The modification is based on chemical characterization tests, namely the equilibrium swelling experiment, to measure the crosslink density evolution. Thus, we obtain the free energy in the aged material based on chemical characterization tests. The developed constitutive equation can predict the mechanical responses of thermo-chemically aged elastomers independently of any mechanical tests on aged specimens. The paper is organized as follows. The hypothesis to develop the constitutive equation is presented in Section 2. Section 3 presents the validation of the developed constitutive equations versus several sets of independent experimental data available in the literature.

2. Constitutive relationship for thermo-chemically aged elastomers

This section proposes a physics-based constitutive equation to predict the response of thermo-chemically aged elastomers. Based on the obtained fundamental understanding of the physical and chemical changes in the network of elastomers under thermo-chemical aging, summarized in Section 1.1, we neglect the dissipative energies due to chain-scission and crosslink breakage. We assume that the dominant thermo-chemical aging phenomenon is the extra crosslinks formation within the elastomer, which is an energy storage process. Then, the evolution of crosslink density due to thermo-chemical aging is used to acquire the free energy in aged elastomers. To achieve this, we modify the network stiffness and the chain extensibility in the well-known Arruda-Boyce eight-chain model (Arruda & Boyce, 1993) to obtain the free energy of thermo-chemically aged elastomers.

The Arruda-Boyce eight-chain constitutive equation accounts for the non-Gaussian nature of the molecular chain stretch and provides an accurate representation of the large-strain behavior of rubber-like materials under different states of deformation. An attractive feature of the Arruda-Boyce description (besides being micro-mechanically motivated) is that it only requires two physics-based material properties, i.e., the network chain density (or equivalently the rubber shear modulus), and the limiting chain extensibility to capture elastomer behavior under different states of loading (i.e., uniaxial, shear, and biaxial). The Helmholtz free energy according to the incompressible Arruda–Boyce model, Ψ_{AB}, is given by (Arruda & Boyce, 1993)

$$\Psi_{AB}\left(\mathbf{C}\right) = n_0 K_B \Theta N_0 \left[\frac{\lambda_{chain}}{\sqrt{N_0}} \mathcal{L}^{-1}\left(\frac{\lambda_{chain}}{\sqrt{N_0}}\right) + ln \frac{\mathcal{L}^{-1}\left(\frac{\lambda_{chain}}{\sqrt{N_0}}\right)}{sinh(\mathcal{L}^{-1}\left(\frac{\lambda_{chain}}{\sqrt{N_0}}\right))} \right] \tag{1}$$

where $\mathbf{C}$ is the right Cauchy-Green strain tensor, n_0, K_B, and Θ are the number of chains per unit volume, the Boltzmann constant, and the absolute temperature, respectively, N_0 is the number of Kuhn monomers per chain of the elastomer and is related to the limiting chain extensibility λ_{lock} as $N_0 = \lambda_{lock}^2$, $\mathcal{L}(\cdot) = coth(\cdot) - \frac{1}{(\cdot)}$ is the Langevin function whose inverse $\mathcal{L}^{-1}$ is given by several approximations in the literature, among which we find the well-known Pade approximation that is $\mathcal{L}^{-1}(x) = x\frac{3-x^2}{1-x^2}$, and $\lambda_{chain}(\mathbf{C}) = \sqrt{\frac{I_1(\mathbf{C})}{3}}$ is the relative macro-stretch written as a function of the first invariant of the right Cauchy-Green strain tensor $I_1(\mathbf{C}) = tr(\mathbf{F}^T\mathbf{F})$, where $\mathbf{F}$ is the deformation gradient tensor. Note that the dependence of the Arruda-Boyce free energy expression on the first invariant of the right Cauchy-Green tensor makes it an invariant based hyperelastic constitutive equation.

Equation 1 can be written in polynomial form using the first five terms of the inverse Langevin function as

$$\Psi_{AB}(\mathbf{C}) = \mu_0 \sum_{i=1}^{5} c_i \frac{1}{N_0^{2i-2}} \left(I_{1\mathbf{C}}^i - 3^i\right) \tag{2}$$

where $\mu_0 = n_0 K_B \Theta$ is the rubber shear modulus. The constants c_i in Equation 2 are equal to $c_1 = \frac{1}{2}, c_2 = \frac{1}{20}, c_3 = \frac{11}{1050}, c_4 = \frac{19}{7000}, c_5 = \frac{519}{673750}$.

As it has been argued in subsection 1.1, crosslink formation is the dominant mechanism in the thermo-chemical aging of elastomers, and an oxidized product has a more crosslinked network of smaller chains compared to the unaged polymer with the longer crosslinked network (e.g., Konica & Sain (2021)). Therefore, the number of Kuhn monomers per chain in elastomers changes and decreases upon aging. On the other hand, the formation of crosslinks between these newly formed short-chains induces more stiffness as the deformation of short polymer chains in a highly crosslinked material is more difficult. Recognizing that the Arruda-Boyce Helmholtz free energy is indeed a function of two main micro-mechanically motivated material parameters: (1) the rubber shear modulus μ_0 (which increases with respect to aging time) and (2) the number of Kuhn monomers per chain N_0 (which decreases with respect to aging time), the effect of aging on the Helmholtz free energy can be accounted for by describing appropriate evolution functions of μ and N with respect to aging time, i.e., $\mu(t)$ and $N(t)$.

First, motivated by the expression of the shear modulus in Equation 2, $\mu_0 = n_0 K_B \Theta$, we consider that the increase in the number of the newly formed crosslinks per volume due to aging (i.e., crosslink density) directly affects the shear modulus of the material at the corresponding aging state and write a micro-mechanically motivated expression for the evolution of shear modulus, $\mu(t)$, as

$$\begin{aligned}\mu(t) &= n_0 K_B \Theta + \big(\nu(t) - \nu_0\big) R\Theta \\ &= \mu_0 + \big(\nu(t) - \nu_0\big) R\Theta\end{aligned} \tag{3}$$

where ν_0 and $\nu(t)$ are the crosslink densities of the unaged material (at aging time $t = 0$) and the aged material (at some later aging time t), respectively, and R is the natural gas constant. In equation 3, the term $(\nu - \nu_0)$ gives the change in the crosslink density between the primary network configuration and the network configuration corresponding to a given aging state. A stiffness-like component is introduced by multiplying the change in the crosslink density which has units of moles per volume by the natural gas constant R and the absolute temperature Θ.

Second, the conservation of mass principle in polymers requires that the product of shear modulus and the number of Kuhn monomers per chain of the elastomer remain constant, that is $\mu(t)N(t) = \mu_0 N_0$, where $N(t)$ is the number of Kuhn monomers per chain of the elastomer at the current state of aging. Therefore, $N(t)$ can be obtained according to

$$N(t) = \frac{N_0 \nu_0}{\nu(t)} \tag{4}$$

As a result of these two modifications, the free energy of aged elastomer is effectively considered based on the crosslink density evolution. The expected stiffness and Kuhn segment variations upon aging is appropriately accounted for. Therefore, we can re-write the Arruda-Boyce free energy equation for thermo-chemically aged elastomer based on the expressions for $\mu(t)$ and $N(t)$, which are obtained based on macromolecular network evolution, as

$$\Psi_a\left(\mathbf{C}, t\right) = \mu(t) \sum_{i=1}^{5} c_i \frac{1}{N(t)^{2i-2}} \left(I_{1\mathbf{C}}^{i} - 3^{i}\right) \tag{5}$$

where $\mu(t)$ and $N(t)$ are given by Equations 3 and 4, respectively, and Ψ_a is the Helmholtz free energy of the aged material (for some aging time t) combining the contribution from the original elastomer network prior to aging and the contribution of the secondary network formed due to crosslinking. The second Piola-Kirchhoff stress tensor, $\mathbf{S}$, can then be obtained by substituting Equation 5 into $\mathbf{S} = 2\rho \frac{\partial \Psi_a}{\partial \mathbf{C}}$. The first Piola-Kirchhoff stress tensor $\mathbf{P}$ can be computed as $\mathbf{P} = \mathbf{FS}$.

The obtained constitutive equation follows the consistency conditions as: (1) $\Psi_a\left(\mathbf{C}, t\right) = 0$ when $\mathbf{C} = \mathbf{I}$, that is, when a network is in its reference configuration (where no mechanical load or displacement is applied to the unaged or aged material); (2) $\Psi_a\left(\mathbf{C}, t\right) > 0$ when $\mathbf{C} \neq \mathbf{I}$, that is, when a network is deformed; (3) each network is stress free in its reference configuration and the network reformation process occurs stressless.

It should also be mentioned that the original network in the eight-chain model was assumed to be isotropic in its reference configuration and the formation of new network during the application of mechanical loading is neglected. Subsequently, each newly formed crosslink is also assumed to be isotropic in its reference configuration and the formation of new network during the application of mechanical loading is neglected. The assumption of isotropic crosslink formation and network evolution is only made because of the absence of experimental results about the symmetry of new networks. This simplifying assumption should be modified to account for a different material symmetry once new understandings of the network evolution may be found. It also should be mentioned that aging during the curing process (Mahnken, 2013), and possible crack healing in elastomers (Kumar et al., 2018) are out of the scope of this study.

Defining characteristics that make our developed approach distinguishable from the previous works are that, first, the evolution of the shear modulus in our constitutive equation depends directly on the crosslink density achieved at a given aging state, and second, the changes in the number of Kuhn monomers per chain is also considered. Therefore, the developed constitutive equation herein provides a one-to-one mapping between chemically-based quantities and physically-based macroscopic variables. The developed constitutive equation relies on two material properties (i.e., μ_0 and N_0) in addition to the crosslink density evolution data. In the case of using an equation to consider the crosslink density evolution, an s-shape function that requires three model parameters can be used.

A summary of the simplifying assumptions in this work is: (1) the energy storage and crosslinking mechanism is the dominant phenomenon in thermo-chemical aging of elastomers, (2) the elastomer is saturated with oxygen and the energy due to chemical diffusion can be neglected, (3) the chemical reactions occur homogeneously inside the thin samples, (4) temperature does not change locally upon the application of mechanical loading, or is negligible (5) the material is assumed incompressible and isotropic, and (6) the aging process does not depend on the strain. It must be noted that the strain can affect the thermo-chemical aging process; this effect is much more pronounced under dynamic deformation compared to static (Ahagon & Kirino, 2006). It must be noted that most of these assumptions are common among all the constitutive equations, which were developed to simulate thermo-chemical aging in elastomers in the literature (e.g., Shaw et al. (2005); Johlitz & Lion (2013); Mohammadi et al. (2020)). Moreover, the developed constitutive equation in this work can be incorporated into the more complicated diffusion-reaction-based constitutive equations to be fully coupled with the diffusion equations. For example, the Helmholtz free energy herein, which is implicitly a function of extent of reactions, can be used instead of the assumed mechanical Helmholtz free energy in the diffusion and reaction-driven work of Konica & Sain (2020).

The future work of the authors is twofold. First, to incorporate the obtained Helmholtz free energy into a diffusion-reaction and thermodynamic-based framework to simulate a fully coupled thermo-chemo-mechanical aging. Second, to incorporate the effect of chain-scission and energy dissipation for a more accurate representation of aging phenomena based on other chemical characterization tests such as nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR).

3. Validation of the developed thermo-chemical aging constitutive equation

In this section, the prediction of the proposed constitutive equation is validated against a set of experimental data available in the literature to assess its capabilities (Hamed & Zhao, 1999; Zhi et al., 2019; Rezig et al., 2020). This particular set of literature was chosen such that the reported articles contained information about both the crosslink density evolution upon aging and a mechanical response of aged samples.

Two types of elastomer compounds (i.e., SBR and NR) with various carbon black filler fractions were identified. Samples were subjected to thermo-chemical aging at various temperatures ranging from 70°C to 120°C.

First, Hamed & Zhao (1999) reported the evolution of crosslink density and tensile tests for filled and unfilled sulfur-vulcanized SBR and NR. The filled materials included 50 phr of N330 carbon black. The SBR specimens contained an antioxidant, while the NR specimens contained 1 phr of dioctylated diphenylamine. The specimens were subjected to air-oven aging at 100°C for various aging times. All specimens were prepared with an average thickness below the critical thickness to ensure uniform oxidation (thicknesses varied between 0.15 and 0.2 mm). The specimens were subsequently tested in tensile mode under a strain rate of approximately 0.017 s^{-1}. The crosslink densities for the unfilled materials were calculated using the classic Flory-Rehner equation, whereas, for the filled samples, the Kraus modification was employed.

In the second study, Zhi et al. (2019) published the crosslink density evolution as well as tensile test results of a filled SBR for several aging times. Vulcanized SBR 1502 (styrene content: 23.5 wt%) sheets that are 2 mm thick were used. The samples contained 50 phr of N330 carbon black. The SBR samples were thermally aged in an air-circulated oven at 120°C. The monotonic stretching tests on aged samples were conducted at a strain rate of 0.06 s^{-1}.

In the last study, Rezig et al. (2020) reported crosslink density evolution for a filled SBR aged under an accelerated aging process at different temperatures and for different exposure times. The investigated material was a vulcanized SBR with 34 phr of sulfur compounds and filled with 34 phr of carbon black. The thickness of the specimens used was 2 mm. Tensile mechanical test results were conducted under a strain rate of 0.005 s^{-1} and were reported for all aging times.

In the following for each data set, the two mechanical material parameters, μ_0 and N_0, were first obtained based on the unaged tensile experimental data and the one-dimensional uniaxial Arruda-Boyce constitutive equation. Table 1 presents the values for μ_0 and N_0 corresponding to each particular unaged elastomer compound. Then, the evolution of the crosslink density obtained experimentally for various elastomers was used to predict the stress-strain responses based on Equations 3–5 and the first

Piola-Kirchhoff stress definition. The average prediction error for each aging duration and each elastomer compound was calculated according to

$$\text{Average error} = \text{average}\left(\frac{\text{experimental data} - \text{model prediction}}{\text{experimental data}}\right) \times 100 \tag{6}$$

where the experimental data and model prediction are data points calculated at select strain levels in the stress-strain response.

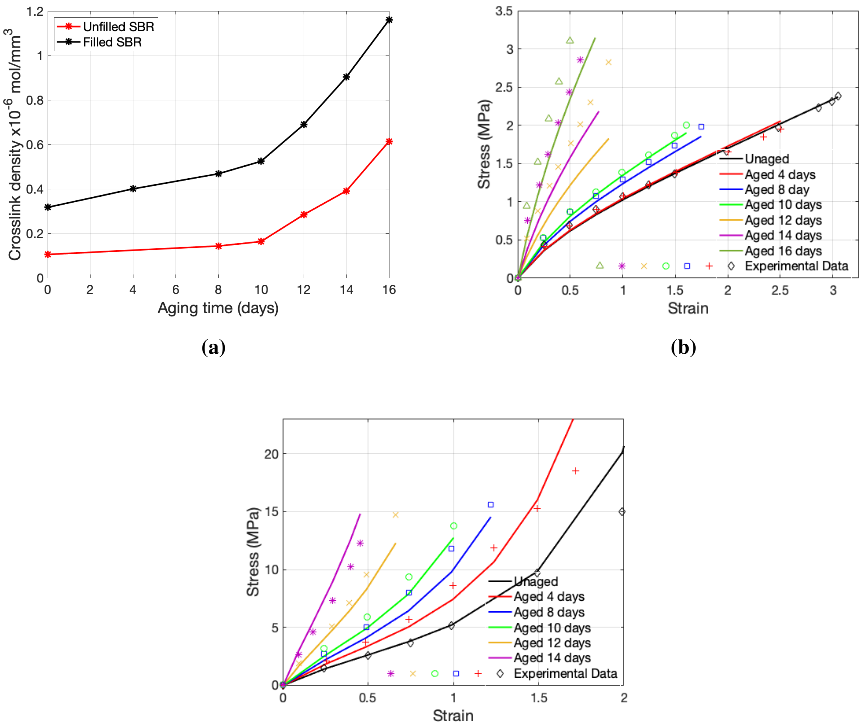
Table 1. The shear modulus and the number of Kuhn monomers per chain for the unaged elastomers obtained by fitting the Arruda-Boyce eight-chain constitutive equation to the unaged stress-strain curves.

	Hamed & Zhao (1999) (T=100°C)			
	Unfilled SBR	Filled SBR	Unfilled NR	Filled NR
μ_0 (MPa)	0.58	1.79	0.5	2
N_0	140	2.961	11.5	4.5
	Zhi et al. (2019)	Rezig et al. (2020)		
	T=120°C	T=100°C	T=90°C	T=70°C
μ_0 (MPa)	0.64	0.58	1.79	0.5
N_0	1.5	140	2.961	11.5

3.1. SBR

In this section, the available data in the literature are used to predict the uniaxial tensile stress-strain responses of unfilled and filled SBR based on their crosslink density evolution upon aging. Figures 1, 2, and 3 demonstrate the prediction of the developed constitutive equation for SBR materials corresponding to the studies of Hamed & Zhao (1999), Zhi et al. (2019), and Rezig et al. (2020), respectively. For each study and its corresponding figure, both the crosslink density evolution as well as the model predictions are presented. Moreover, the average calculated errors using Equation 6 are also summarized in Table 2 and plotted in Figure 4. The cases where the prediction underestimates the experiment are written in red, and where the prediction overestimates the experiments in blue.

It can be observed in Figure 1 that the evolution of the crosslink density follows the same pattern as the change in stiffness for each given aging state wherein the modulus



(a) **(b)**

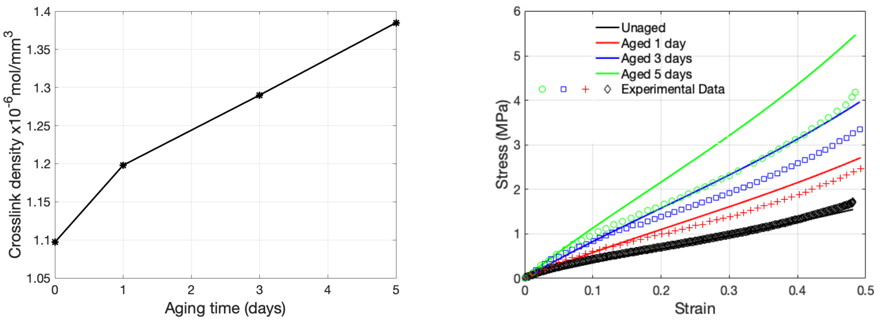
(c)

Fig. 1. a) Crosslink density evolution, and predictions of the developed constitutive equation for different aging times of b) unfilled SBR and c) filled SBR (containing 50 phr carbon black filler)

. The specimen were aged at 100°C for different aging times. The experimental data were reproduced based on Hamed & Zhao (1999).

evolves in accordance with the change in the crosslink density. The modulus – or equivalently stiffness – increases substantially after an initial aging time, mimicking the behavior observed for the crosslink density. The parallelism in the evolution of the elastomer's crosslink density and its corresponding stiffness reinforces the argument that crosslinking reactions are more dominant during thermo-chemical aging.

Moreover, regarding the Hamed & Zhao (1999) unfilled SBR data, it can be seen that errors remain below 10% for the lower aging times (i.e., up to 10-day aging). As the aging time increases, the response for the unfilled SBR predicted by the proposed



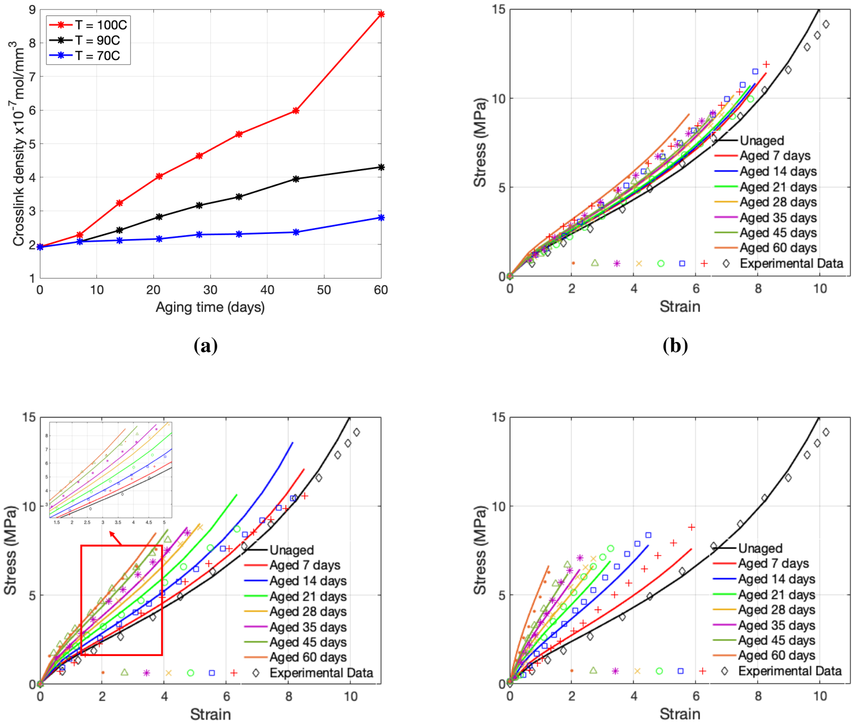
(a) **(b)**

Fig. 2. a) Crosslink density evolution as a function of the aging time and b) predictions of the developed constitutive equation. The specimens were made of filled SBR with 50 phr carbon black and were aged at 120°C for different times.

The experimental data were reproduced based on Zhi et al. (2019).

constitutive equation underestimates the experimental observations. To understand the reason behind this underestimation, it is worth recognizing that during thermo-chemical aging processes, two types of reactions can participate: reaction of free radicals (i.e., alkyl and alkoxy) with $-C{=}C-$ bonds during propagation step and reaction of radicals among themselves during termination step as shown in Figure 5 (Mohammadi & Dargazany, 2019; Le Gac et al., 2016). The underestimation for the unfilled SBR could likely be attributed to the fact that the proposed constitutive equation does not account for the additional molecular chain segments that have been created between free radicals and double carbon $-C{=}C-$ bonds (strong segments in Figure 5. These additional chain segments possess the same load-resisting capacity as the original network chains (albeit shorter in length) and contribute to an increase in the chain density in the unfilled elastomer. Instead, from what it appears, the proposed constitutive relationship accounts for the radical-radical crosslinking reactions which create weaker segments in the unfilled elastomer that do not exhibit the same load resistance as the radical-double bond segments, therefore leading to the underestimation observed.

On the other hand, the predicted response for the case of Hamed & Zhao (1999)'s

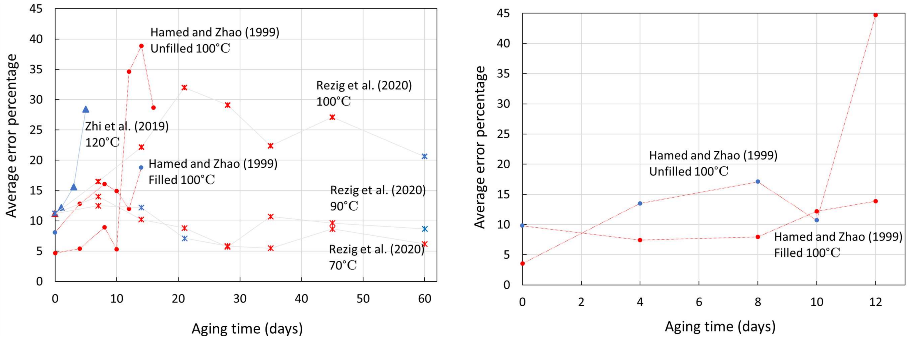


(a) **(b)**

(c) **(d)**

Fig. 3. a) Crosslink density evolution as the aging time at different temperatures for a filled SBR elastomer (the specimens contained 34 phr carbon black); and predictions of the developed constitutive equation for different aging time for the cases when the aging temperature is equal to b) 70°C, c) 90°C, and d) 100°C. The experimental data were reproduced based on Rezig et al. (2020).

filled SBR – which contains 50 phr of carbon black – is quite accurate even at higher aging times. The inclusion of carbon black inhibits radical reactions with $-\mathrm{C}{=}\mathrm{C}-$ bonds and thus reduces the potential of creating additional chain segments between the corresponding junction ends. At the same time, however, carbon black increases the probability of recombination of primary macro-radicals and promotes the creation of additional crosslinks in the material. This is consistent with arguments provided in the literature, which suggest that carbon black acts as a free-radical scavenger capable of binding macro-radicals generated during oxidation (Janowska & Rybiński, 2008; Hamed & Zhao, 1999). Those additional load-resisting chain segments manifested for



(a) **(b)**

Fig. 4. Average error percentage associated with (a) all the SBR cases, and (b) all the NR cases. The Hamed & Zhao (1999)'s filled SBR and the Zhi et al. (2019) cases contained 50 phr carbon black, whereas the Rezig et al. (2020)'s specimens included 34 phr carbon black. Red indicates underestimation whereas blue indicates overestimation.

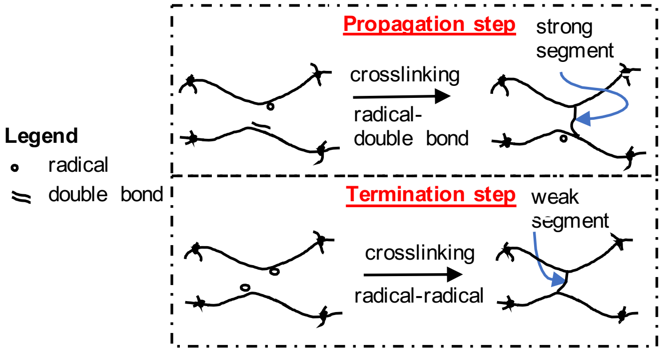


Fig. 5. Schematic for the two types of crosslink reactions: first between radical-double bonds during propagation step and second between radical-radical during termination step. The former results in stiff, load-carrying crosslinked segments that contribute to an increase in stiffness and are denoted here as "strong segments" while the latter results in weaker crosslinked bonds that do not possess as much load-carrying capacity and therefore labeled "weak segments". The proposed constitutive equation appears to account for the radical-radical reaction type. The schematic is developed based on the experimental result of Le Gac et al. (2016).

the unfilled SBR are therefore absent for the filled SBR. The increase in the density of crosslinks at radical-radical junctions is the major contributor to the stiffening behavior of filled SBR, as is properly accounted for by the proposed constitutive relationship.

The overestimation in the longest aging time of the filled SBR (i.e., 14 days) can be explained by the fact that the current model neglects temperature-dependent dissipation mechanisms such as viscoelasticity and other degradation events such as extended chain-scission. The effects of chain-scission become more pronounced by increasing the aging time.

Figure 2 demonstrates the crosslink density evolution and the comparison of prediction versus experiments of Zhi et al. (2019). The overestimation of the experiments can also be observed in this case as well, where the specimens were aged at 120°C. Thus, although the SBR used in Zhi et al. (2019)'s study contains the same carbon black volume fraction as the one used in Hamed & Zhao (1999), the difference in the calculated average errors between the two studies is attributed to the increased aging temperature (i.e., 100°C compared to 120°C). Nevertheless, it is worth mentioning that the experimental stress-strain responses corresponding to the work of Zhi et al. (2019) focused on the lower stress-strain intervals as opposed to the other works where the authors presented the complete stress-strain behavior. The lack of the complete nominal stress-strain behavior could potentially have affected our prediction results.

Figure 3 illustrates the evolution of crosslink density and the predictions of the Rezig et al. (2020) data at three different aging temperatures of 70°C, 90°C, and 100°C. It can be observed that the aging temperature also affects the prediction capability of the proposed constitutive equation. The proposed constitutive equation can replicate the filled SBR's experimental responses very well for the lower aging temperatures (i.e., 70°C, 90°C). In fact, the average error remains below 13% and 14% when the aging temperature is 70°C and 90°C, respectively. The errors, then, increase for the case of higher aging temperature (i.e., 100°C). At the longest aging time of the highest aging temperature (i.e., 60 days aging at 100°C), the constitutive equation overestimates the response of filled SBR in the Rezig et al. (2020) tests. The overestimation is similar to the one observed for the longest aging time of filled SBR in Hamed & Zhao (1999) experiments. The overestimation can be explained similarly in that the current model neglects temperature-dependent dissipation mechanisms, and chain-scission and crosslink breakage likely become more considerable at higher aging conditions.

It is critical to note that the effects of carbon black on the predictions are consistent in the three independent data set results. The SBR utilized in the Rezig et al. (2020)'s study contained 34 phr of carbon black, and therefore, represents an intermediate value between those corresponding to the SBR materials used in Hamed & Zhao (1999) (i.e., 0 phr for unfilled and 50 phr for filled). At the same aging temperature of 100°C, the average errors predicted for this intermediate carbon black fraction fall between those obtained for the cases where the carbon black was 0 and 50 phr. To reiterate, the error associated with Rezig et al. (2020)'s data aged at 100°C, which contains 34 phr carbon black falls between the errors associated with unfilled and 50 phr filled SBR in Hamed & Zhao (1999)'s data. In other words, the average error decreases with an increase in the carbon black volume fraction, thus reinforcing the argument that at higher carbon black contents the potential of additional load-resisting chains forming due to aging reduces, and the number of crosslinks per elastomer volume increases. However, with the increase of aging time, possible dissipation mechanisms such as chain scission cause overestimation. More experimental data is required with different percentages of carbon black filler and aging time and temperature to confirm this hypothesis fully.

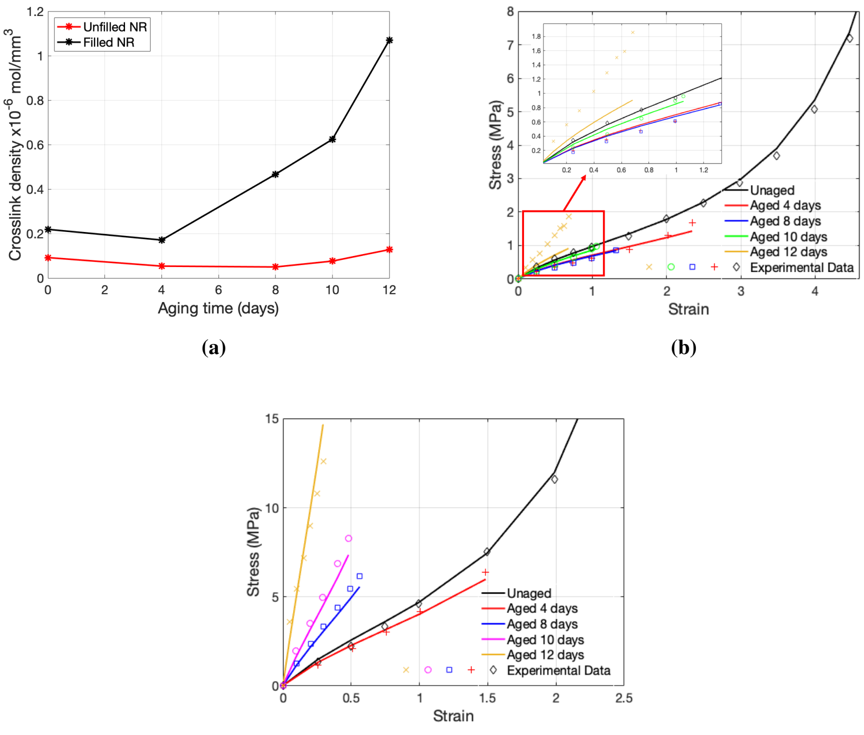
In summary, it can be concluded that the proposed constitutive relationship is most accurate for predicting the response of carbon black-filled elastomers. Specifically, prediction accuracy increases with an increase in filler content and a decrease in aging temperature. The errors associated with filled SBR in all three independent data sets are below 32%. The average of all errors for the filled SBR cases aged at 90°C-120°C (excluding 70°C where the errors are very low) is 16%. The high accuracy associated with filled elastomer prediction is due to the following reason. The increase in the density of crosslinks at radical-radical junctions is the major contributor to the stiffening behavior observed for filled SBR. That is, the potential for forming new load-resisting macromolecular chains is reduced for filled elastomers compared to their unfilled counterparts. As a result, since the proposed constitutive equation properly accounts for the newly created radical-radical segments, prediction accuracy for the case of filled elastomers is high. As the aging temperature exceeds 100°C, the effects of temperature-dependent dissipation mechanisms such as viscoelasticity or other molecular dissipation events such as extended chain-scission events become more dominant, and the prediction using the proposed model is overestimated, although the errors still remain within a reasonable low-limit range.

3.2. NR

In this section, the capability of the proposed constitutive equation in predicting the tensile stress-strain responses of unfilled and filled NR at various aging states (Hamed & Zhao, 1999) is outlined. Figure 6 demonstrates the evolution of the crosslink density for both unfilled and filled NR as well as the corresponding model predictions compared to the experimental results. It can be seen that the developed constitutive equation can predict the responses very well regardless of whether the material stiffens or softens. As evidenced by Figure 6b, unfilled NR undergoes an extended period of softening up to 10 days. During this aging stage, the crosslink density diminishes compared to the initial unaged state. The dependence of the stiffness parameter on the crosslink density makes it possible for the constitutive equation to capture the case when the material actually softens (i.e., the case where network chain disruption events are greater than its formation counterparts). Additionally, similar to the behavior observed regarding the effect of carbon black on SBR's predictions, the predicted responses for the filled NR are more accurate compared to the unfilled NR at higher aging duration. In fact, the highest calculated error for filled NR was approximately 13.9% for the 12-day aging time (compared to about 44% for the unfilled NR at the same aging time).

3.3. Discussion

The proposed constitutive equation can, given the evolution of the crosslink density, predict the mechanical responses of aged elastomeric materials fairly well even when only two material parameters are employed – in this case, the rubber shear modulus and the number of Kuhn monomers per chain of the unaged elastomer within the Arruda-Boyce eight-chain constitutive theory. The ability of the constitutive equation to accurately predict the mechanical test results of aged materials independently of any mechanical tests, i.e., without conducting any further fitting to the experimental test results on aged samples, constitutes an attractive feature of the proposed relationship. The average reported errors in this study with the low number of model parameters is unprecedented in the literature. Many, if not all of the existing works in the literature,



(a)

(b)

(c)

Fig. 6. a) Crosslink density evolution as the aging time, and predictions of developed constitutive equation for different aging time of b) unfilled NR and c) filled NR (contained 50 phr carbon black)

. The experimental data were reproduced based on Hamed & Zhao (1999).

use several mechanical tests to fit and obtain numerous model parameters associated with their constitutive equations.

For example, Johlitz et al. (2014)'s phenomenological constitutive equation is based on the Mooney-Rivlin hyperelastic theory and contains fourteen model parameters. Their constitutive model, which is based on the concept of state variables considering network scission and reformation events, requires two sets of mechanical experimental tests for different aging conditions for calibration. Moreover, recently, Mohammadi et al. (2020) used three to six parameters for an Arrhenius-based aging decay function. In addition to the Arrhenius-based aging decay function parameters, seven mechanical model parameters were used to fit the experimental observations. Their average errors at T=95°C, which were deemed acceptable, were computed to be 5.75%, 21.55%, 23.52%, and 12.01% for the unaged, one-day, five-day, and ten-day aging times, respectively. Since our average error range falls below these values, it can be argued that the developed constitutive equation herein yields acceptable predictions even when very few material properties and tests are utilized. Moreover, most kinetics models available in the literature employ a series of model parameters to describe only one mechanism at a time (e.g., either when the aged material is softer than its unaged configuration or vice-versa). Doing so results in a large number of variables to appropriately consider all cases of network evolution, such as in the case of Lion & Johlitz (2012). The crosslink density evolution approach adopted in this work bypasses the need for incorporating more material parameters than necessary and yields reasonable estimations of the response of aged elastomers, especially for the case of carbon black-filled elastomers. The proposed constitutive equation avoids the need for conducting further mechanical tests and provides predictions of the responses of aged materials within reasonable accuracy using only two material parameters corresponding to the unaged configuration in addition to one chemical characterization test.

4. Conclusions

A physics-based constitutive equation for the mechanical responses of thermo-chemically aged elastomers has been proposed in this paper. The constitutive equation is based on modifying the Helmholtz free energy in the material upon aging. To achieve this, the effect of network crosslink reformation in modifying the shear modulus and chain segments is considered. The modification is based on chemical characterization tests, namely equilibrium swelling experiment, to measure the crosslink density evolution. The developed constitutive equation can predict the mechanical responses of thermo-chemically aged elastomers independently of mechanical tests on aged specimens within reasonable accuracy. The main contribution of this work is to connect the form of stored energy directly to chemical characterization experiments. Unlike all previous studies, instead of conjecturing and assuming the form of energy storage, in

Table 2. Associated average errors obtained by comparing the predicted stress-strain results based on Equations 3-5 and experimental tensile test results. Numbers in red indicate that the constitutive relationships underestimated the experimental results, whereas numbers in blue show overestimation.

Hamed & Zhao (1999) SBR (T=100°C)

	Unaged	4-day	8-day	10-day	12-day	14-day	16-day
Unfilled	4.68	5.42	8.94	5.33	34.6	38.9	28.7
Filled	8.09	12.8	16.1	14.9	12.0	18.8	–

Zhi et al. (2019) SBR (T=120°C)

	Unaged	1-day	3-day	5-day
	11.18	12.2	15.6	28.4

Rezig et al. (2020) SBR (T=100°C)

Unaged	7-day	14-day	21-day	28-day	35-day	45-day	60-day
11.2	16.5	22.2	32.0	29.1	22.4	27.1	20.6

Rezig et al. (2020) SBR (T=90°C)

Unaged	7-day	14-day	21-day	28-day	35-day	45-day	60-day
11.2	12.5	12.2	7.13	5.86	5.48	8.67	6.19

Rezig et al. (2020) SBR (T=70°C)

Unaged	7-day	14-day	21-day	28-day	35-day	45-day	60-day
11.2	14.02	10.2	8.83	5.69	10.7	9.62	8.69

Hamed & Zhao (1999) NR (T=100°C)

	Unaged	4-day	8-day	10-day	12-day
Unfilled	3.57	13.5	17.1	10.7	44.7
Filled	9.82	7.46	7.97	12.2	13.9

this work, we develop a robust approach to obtain the stored energy as a function of crosslink formation. The proposed constitutive relationship thus provides a one-to-one mapping between chemically-based quantities (i.e., crosslink density) and physically-based macroscopic variables (i.e., shear modulus and chain extensibility).

Comparison with experimental results showed that for the set of commercially available elastomers; more specifically filled and unfilled SBR and NR; the crosslink formation is the dominant network evolution. For the temperature range of up to 100°C and up to 16 days, the Helmholtz free energy based on the crosslink formation can accurately predict the mechanical responses of thermo-chemically aged elastomers. The average error for all the cases of SBR (filled and unfilled) aged at 100°C is 18.6% where the maximum error, 38.9%, belongs to a case of an unfilled SBR. However, the average error for all the filled SBR cases is 16%. By increasing the temperature above 100°C, the rate of chain scission rapidly increases, and energy dissipation must be taken into account for accurate predictions. It should be emphasized that verification in this work was conducted versus two types of elastomer with different rubber compositions, which enhances the reliability of the developed constitutive equations.

The developed constitutive equation in this work can be easily incorporated into a more complicated diffusion-reaction-based constitutive framework to be fully coupled with the diffusion equations. The physically-based Helmholtz free energy proposed in this work can be used instead of phenomenologically assumed mechanical Helmholtz free energy in previous works, where the comprehensive reaction-driven Clausius-Duhem inequality were derived. This integration is the topic of future work by the authors. Therefore, in the future, we will try to release the simplifying assumption used in this work. First, we will add the diffusion equation and consider the full thermo-chemical aging coupling instead of simulating the mechanical response of the thermo-chemically aged elastomers. Second, we will incorporate the effect of deformation on the aging process as well as the damage and fracture response.

Acknowledgment

The authors gratefully acknowledge the support from the National Science Foundation under the award number CMMI-1914565 and the Air-Force Office of Scientific Research (AFOSR) Young Investigator Program (YIP) award #FA9550-20-1-0281.

References

Achenbach, M., & Duarte, J. (2003). A finite element methodology to predict age-related mechanical properties and performance changes in rubber components. *Constitutive Models for Rubber*, (pp. 59–70).

Ahagon, A., & Kirino, Y. (2006). Aging of black filled rubber under deformation. *Rubber chemistry and technology*, *79*, 641–652.

Arruda, E. M., & Boyce, M. C. (1993). A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials. *Journal of the Mechanics and Physics of Solids*, *41*, 389–412.

Beurle, D., André, M., Nackenhorst, U., & Desmorat, R. (2020). Micromechanically motivated model for oxidation ageing of elastomers. In P. Wriggers, O. Allix, & C. Weißenfels (Eds.), *Virtual Design and Validation* (pp. 271–290). Cham: Springer International Publishing.

Blum, G. W., Shelton, J. R., & Winn, H. (1951). Rubber oxidation and aging studies safe limits of sample thickness. *Rubber Chemistry and Technology*, *24*, 999–1016.

Celina, M., Graham, A. C., Gillen, K. T., Assink, R. A., & Minier, L. M. (2000a). Thermal degradation studies of a polyurethane propellant binder. *Rubber Chemistry and Technology*, *73*, 678–693.

Celina, M., Wise, J., Ottesen, D., Gillen, K., & Clough, R. (1998). Oxidation profiles of thermally aged nitrile rubber. *Polymer Degradation and Stability*, *60*, 493–504.

Celina, M., Wise, J., Ottesen, D., Gillen, K., & Clough, R. (2000b). Correlation of chemical and mechanical property changes during oxidative degradation of neoprene. *Polymer Degradation and Stability*, *68*, 171 – 184.

Celina, M. C. (2013). Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polymer Degradation and Stability*, *98*, 2419–2429.

Dal, H., & Kaliske, M. (2009). A micro-continuum-mechanical material model for failure of rubber-like materials: Application to ageing-induced fracturing. *Journal of the Mechanics and Physics of Solids*, *57*, 1340–1356.

Gigliotti, M., Grandidier, J., & Lafarie-Frenot, M. (2011). Assessment of chemo-mechanical couplings in polymer matrix materials exposed to thermo-oxidative environments at high temperatures and under tensile loadings. *Mechanics of Materials*, *43*, 431 – 443.

Gillen, K. T., Wise, J., & Clough, R. (1995). General solution for the basic autoxidation scheme. *Polymer Degradation and Stability*, *47*, 149 – 161.

Hamed, G., & Zhao, J. (1999). Tensile behavior after oxidative aging of gum and black-filled vulcanizates of sbr and nr. *Rubber chemistry and technology*, *72*, 721–730.

Hossain, M., & Steinmann, P. (2015). Continuum physics of materials with time-dependent properties: reviewing the case of polymer curing. *Advances in Applied Mechanics*, *48*, 141–259.

Hutchinson, J. M. (1995). Physical aging of polymers. *Progress in Polymer Science*, *20*, 703 – 760.

Janowska, G., & Rybiński, P. (2008). Influence of carbon black on thermal properties and flammability of cross-linked elastomers. *Journal of thermal analysis and calorimetry*, *91*, 697–701.

Johlitz, M., Diercks, N., & Lion, A. (2014). Thermo-oxidative ageing of elastomers: A modelling approach based on a finite strain theory. *International Journal of Plasticity*, *63*, 138 – 151.

Johlitz, M., & Lion, A. (2013). Chemo-thermomechanical ageing of elastomers based on multiphase continuum mechanics. *Continuum Mechanics and Thermodynamics*, *25*, 605–624.

Johlitz, M., Retka, J., & Lion, A. (2011). Chemical ageing of elastomers: experiments and modelling. *Constitutive Models for Rubber VII*, *7*, 113–118.

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.

Konica, S., & Sain, T. (2021). A reaction-driven evolving network theory coupled with phase-field fracture to model polymer oxidative aging. *Journal of the Mechanics and Physics of Solids*, *150*, 104347.

Kumar, A., Francfort, G., & Lopez-Pamies, O. (2018). Fracture and healing of elastomers: A phase-transition theory and numerical implementation. *Journal of the Mechanics and Physics of Solids*, *112*, 523–551.

Le Gac, P. Y., Celina, M., Roux, G., Verdu, J., Davies, P., & Fayolle, B. (2016). Predictive ageing of elastomers: Oxidation driven modulus changes for polychloroprene. *Polymer Degradation and Stability*, *130*, 348–355.

Lejeunes, S., Eyheramendy, D., Boukamel, A., Delattre, A., Méo, S., & Ahose, K. (2018). A constitutive multiphysics modeling for nearly incompressible dissipative materials: application to thermo–chemo-mechanical aging of rubbers. *Mechanics of Time-Dependent Materials*, *22*, 51–66.

Lion, A., & Johlitz, M. (2012). On the representation of chemical ageing of rubber in continuum mechanics. *International Journal of Solids and Structures*, *49*, 1227 – 1240.

Mahnken, R. (2013). Thermodynamic consistent modeling of polymer curing coupled to visco–elasticity at large strains. *International Journal of Solids and Structures*, *50*, 2003 – 2021.

Mohammadi, H., & Dargazany, R. (2019). A micro-mechanical approach to model thermal induced aging in elastomers. *International Journal of Plasticity*, *118*, 1–16.

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*, *175*, 109108.

Pochiraju, K., & Tandon, G. (2006). Modeling thermo-oxidative layer growth in high-temperature resins. *Journal of Engineering Materials and Technology*, *128*, 107–116.

Rezig, N., Bellahcene, T., Aberkane, M., & Nait Abdelaziz, M. (2020). Thermo-oxidative ageing of a sbr rubber: effects on mechanical and chemical properties. *Journal of Polymer Research*, *27*, 339.

Shakiba, M., Darabi, M., & Al-Rub, R. K. A. (2016). A thermodynamic framework for constitutive modeling of coupled moisture-mechanical induced damage in partially saturated viscous porous media. *Mechanics of Materials*, *96*, 53 – 75.

Shakiba, M., Darabi, M. K., Al-Rub, R. K. A., Masad, E. A., & Little, D. N. (2014). Microstructural modeling of asphalt concrete using a coupled moisture-mechanical constitutive relationship. *International Journal of Solids and Structures*, *51*, 4260 – 4279.

Shaw, J. A., Jones, A. S., & Wineman, A. S. (2005). Chemorheological response of elastomers at elevated temperatures: Experiments and simulations. *Journal of the Mechanics and Physics of Solids*, *53*, 2758 – 2793.

Steinke, L., Veltin, U., Flamm, M., Lion, A., & Celina, M. (2011). Numerical analysis of the heterogeneous ageing of rubber products. *Constitutive Models for Rubber VII*, *7*, 155–160.

Tobolsky, A. V., Prettyman, I. B., & Dillon, J. H. (1944). Stress relaxation of natural and synthetic rubber stocks. *Rubber Chemistry and Technology*, *17*, 551–575.

Wineman, A. (2009). On the mechanics of elastomers undergoing scission and cross-linking. *International Journal of Advances in Engineering Sciences and Applied Mathematics*, *1*, 123–131.

Wineman, A., & Shaw, J. (2019). Coupled thermal- and deformation-induced degradation in planar rubber membranes under radial loading. *Mathematics and Mechanics of Solids*, *24*, 3103–3124.

Wise, J., Gillen, K., & Clough, R. (1995). An ultrasensitive technique for testing the arrhenius extrapolation assumption for thermally aged elastomers. *Polymer Degradation and Stability*, *49*, 403–418.

Wise, J., Gillen, K., & Clough, R. (1997a). Quantitative model for the time development of diffusion-limited oxidation profiles. *Polymer*, *38*, 1929 – 1944.

Wise, J., Gillen, K. T., & Clough, R. L. (1997b). Time development of diffusion-limited oxidation profiles in a radiation environment. *Radiation Physics and Chemistry*, *49*, 565 – 573.

Zhi, J., Wang, Q., Zhang, M., Zhou, Z., Liu, A., & Jia, Y. (2019). Coupled analysis on hyper-viscoelastic mechanical behavior and macromolecular network alteration of rubber during thermo-oxidative aging process. *Polymer*, *171*, 15–24.