Material Property Characterization for Elastomers within the Framework of Finite-Deformation Viscoelasticity

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Abstract

Elastomers are polymeric materials that consist of highly mobile long-molecule chains jointed together through crosslinking. The behavior of elastomers is commonly manifested by hyperelasticity and viscosity due to their molecular structure. Any variation of the material microstructure may have an impact on the macroscopic properties of elastomers. Therefore, characterizing the material properties of elastomers with appropriate constitutive models is essential to facilitating their potential applications. Although various constitutive models have been developed to describe the hyperelastic and viscoelastic behaviors of elastomers, it is still challenging to quantify the material properties of elastomers since there exist restrictions and limitations of the constitutive models. This thesis work attempts to develop a material property characterization package that consists of a constitutive model database and the corresponding selection strategy. The constitutive model database is established by adopting various constitutive models to the continuum mechanics framework with the incorporation of nonlinear material viscosity based on polymer dynamics. The feasibility and capability of the material property characterization package is validated by the commonly used filled and unfilled elastomers under different loading conditions, demonstrating a good agreement between the theoretical predictions of the material response and the experimental data. The developed framework is expected to work as a general platform for material property characterization of elastomeric materials.

Keywords

Elastomer; Hyperelasticity; Finite-deformation viscoelasticity; Nonlinear viscosity; Material property characterization.
Summary for Lay Audience

Elastomers are widely used in many areas, including automobiles, aerospace, consumer products, industrial products, medical products, etc. Due to their molecular structure, elastomers are characterized by the capability of sustaining large deformation, which enables their potential applications in the cutting-edge fields of actuation, soft robotics, biomimetics, and energy harvesting in addition to daily uses. The advancement of various applications is contingent on a better understanding of the hyperelastic and viscoelastic behaviors of elastomers, which have gained extensive attention from the research community.

In the literature, various constitutive models have been proposed to characterize the hyperelastic and viscoelastic behaviors of elastomers under different loading conditions. As these constitutive models are developed based on different hypotheses, they may have certain limitations in capturing the material responses of elastomers. It is also found that any variation of the material microstructure, such as chemical composition, degree of polymerization, extensibility of polymer chains, molecular weight of polymer chains, cross-linking density, and amount of chain entanglement, may have an essential impact on the overall properties of elastomers. To facilitate the full potential applications of elastomers, it is essential to find appropriate constitutive models to quantify the material responses. It is therefore the objective of this thesis to develop a material property characterization package for constitutive model selection and material properties identification. Validated by three commonly used elastomers, the developed material property characterization package is expected to establish a general platform for the material property characterization of new elastomeric materials.
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Chapter 1

1 Introduction

1.1 Elastomers

Polymers have a molecular structure comprised of long-molecule chains with repeated smaller units called monomers. Elastomers, with exchangeable name of rubbers, are special polymeric materials in which polymer chains are held together by relatively weak intermolecular bonds. These long polymer chains in elastomers are crosslinked through crosslinkers or radiation, resulting in a “spaghetti and meatball” structure as shown in Figure 1-1. Elastomers are commonly characterized as hyperelastic and viscous materials with low elastic modulus and high failure strain in comparison with some other materials. The hyperelasticity originates from the strong and flexible cross-linked long chains which possess the capability of reconfiguration to distribute stress and returning to the original shape when the stress is removed even under large deformation, while the viscosity mainly attributes to the reptation of diffusive polymer chains. Elastomers can be classified into two major categories, unsaturated rubbers which can be cured by sulfur or non-sulfur vulcanization and saturated ones that cannot be cured by sulfur vulcanization. They have extensive applications in many areas, including consumer products, industrial products, medical products, constructions, automobiles, etc. Some commonly used elastomers include silicone (medical prosthetics, molds, lubricants, baby pacifiers, adhesives and sealants), natural rubbers (automotive parts and shoe soles), neoprene (wires and cables and some other insulating materials), polybutadiene (vehicle tires), and polyurethanes (elastic clothing fabric and sealing materials), just to name a few [1]. With the recent advancement of the cutting-edge transduction technology, dielectric elastomers have been widely used in the fields of artificial muscles [2-4], soft robots [5-6], different types of actuators [7-8], energy harvesters [9-10] and so on.
1.2 Characteristics and applications of elastomers

Hyperelasticity is the predominant characteristics of elastomers, i.e., the material possesses the capability of elastic recovery even after large deformation. This is one of the main reasons that elastomers are widely used for actuation purpose [1]. Viscosity is also an intrinsic nature of most elastomers, which enable the applications of elastomers for fabricating anti-vibration products such as dampers, vibration isolators, and shock absorbers [5, 11-12]. Discovered in the 18th century, rubbers were first used to produce waterproof coatings of shoes by locals of South America as they were characterized with excellent sealing ability [13]. Due to such sealant effect, rubbers are also widely used to manufacture gaskets, steam hoses and oil pipes. As elastomers are also characterized to possess good fracture toughness and better abrasion resistance than metals, they are often used in automotive parts and industrial facilities [13]. Due to the biocompatibility and the superior thermal and chemical resistance, silicones are widely used as medical products. Some elastomers, like rubbers, are capable of adhering to most other materials, which enables manufacturing the elastomer-based hybrid materials. The combination with different reinforcing fillers can harness the distinctive and, at the same time, complementary merits of each material. For example, with the addition of fibers like rayon, polyester, metal and glass, the mechanical tensile strength of the elastomer-based composite will be significantly improved with a compromise in extensibility [13].

Some elastomers are sensitive to electric stimulus, demonstrating dielectric property. These dielectric elastomers have aroused widespread interests in the research and industrial fields due to their combined electromechanical coupling and capability of sustaining large...
deformation, particularly for the applications in transduction technology. Moreover, dielectric materials are also characterized with low density, low cost, high energy density and high-speed response [14-15]. Such good overall performance enables dielectric elastomers as more desirable materials to fabricate actuators, which can be generally used as switches, soft robotics, electronics and various automation devices, just to name a few [6, 11-12]. For example, elastomers are used to make artificial tissues since they are soft in nature, biocompatible with human body and capable of deforming in response to electrical stimulus. Electrical signals generated from the brain control the change in configuration of human organs, such as the beating of heart, the expanding and contracting of blood vessels, and motions performed by four limbs. Dielectric elastomers are also capable of collecting energy in a simple way of stretching and contracting from natural sources including ocean weaves, flowing water, blowing wind, and human activities like walking and running [10]. In combination with the large deformation capability, high energy density, good electromechanical conversion efficiency and low cost, dielectric elastomers are regarded promising candidates for a wider range of energy harvesting applications, at both small-scale and large-scale [7, 16].

1.3 Influence of microstructure on macroscopic properties

The macroscopic properties of elastomers depend on their microstructures, i.e., the molecular structure of elastomers. As discussed in the first section, the hyperelasiticity of elastomers originates from the crosslinked ground network, while the viscosity is attributed to the diffusion of the highly mobile polymer chains as represented by the subnetworks in the parallel rheological model. Any variation in the physics and chemistry parameters of the molecular structure of elastomers, such as chemical composition, degree of polymerization, extensibility of polymer chains, molecular weight of polymer chains, cross-linking density, and amount of chain entanglement, may have an essential impact on the overall properties of the material. For example, highly crosslinked elastomers have a higher shear modulus than coarsely crosslinked elastomers above the glass transition temperature [17]. The higher entanglement density increases the tensile strength of elastomers since there are more molecular chains to support the stress [18]. Increasing the degree of polymerization correlates to a higher melting temperature of elastomers [19]. The
high molecular weight is associated with better resistance against crack and abrasion [20]. It is evident from these examples that the macroscopic properties of elastomers can be adjusted by tailoring the microstructure. In order to fulfill the potential applications of elastomers, particularly with the development of new elastomeric materials, it is essential to characterizing the material properties to further understand their viscoelastic behavior.

1.4 Objectives

In the literature, a variety of constitutive models have been developed to capture the hyperelastic nature of elastomers, including the continuum mechanics-based models [21-24] and those from statistical mechanics treatment [25-30]. In attempt to explain the viscous effect of elastomers under finite deformation, extensive research has been conducted to develop viscoelastic constitutive models. Examples include the phenomenological models [31-35], the micromechanism inspired constitutive models [36-39], and the micro-mechanically based models [12, 40-41]. Until recently, Zhou et al. [42] has developed a micro-macro constitutive model for finite deformation of viscoelasticity, which combines the merits of both the micromechanism inspired model and the micro-mechanically based model. It is claimed as a general platform which can be easily implemented in the finite element simulation with the capability of adopting most of the hyperelastic constitutive relations.

As elastomers are usually utilized with complex geometries and under sophisticated loading conditions, finite element analysis has become a necessity in simulating their response and understanding their viscoelastic performance. Appropriate constitutive models with quantified material properties are important prerequisites for proper numerical simulations. The motivation behind the current work originates from the demand for selecting appropriate constitutive models and quantifying the corresponding representative material parameters of elastomers by using the standard experimental data, which will be served as the inputs of the finite element analysis. The long-term goal of this work is to establish a database of material models implemented into the commercial software like ABAQUS, which is capable of capturing material viscoelasticity, large deformation and multiphysics coupling. The objective of the present research is to develop a material
property characterization package for constitutive model selection and material properties identification. To accomplish this purpose, the following work will be conducted:

1. Describing the continuum mechanics framework with the incorporation of the mathematical treatment on the nonlinear viscosity of elastomers under finite deformation.
2. Establishing the material property characterization package by creating a constitutive model database and proposing selection strategy.
3. Validating the capability and feasibility of the material property characterization package with three commonly used elastomers.

The selected constitutive models and the identified material parameters can be used as input of the finite element analysis to predict the viscoelastic response of elastomers with complex geometries and under general loading conditions.

1.5 Thesis structure

Chapter 1 provides a general introduction of elastomers, the motivation, and the objectives of the present work. A comprehensive literature review will be followed in Chapter 2. Chapter 3 outlines the theoretical framework of the material property characterization package, including the continuum mechanics framework for the finite-deformation viscoelasticity with the treatment of nonlinear material viscosity, the establishment of constitutive model database, and the selection procedure for constitutive models. The capability and feasibility of the developed material property characterization package will be validated by three commonly used elastomers as presented in Chapter 4. In the end, Chapter 5 concludes the thesis with recommendations for future study.
Chapter 2

2 Literature Review

To accurately predict the response of elastomers and facilitate their full potential applications, substantial efforts have been devoted to developing constitutive models to capture the intrinsic hyperelasticity and viscosity of the materials, as well as conducting experimental investigations on material property characterization. In this section, a literature review on the relevant experiments conducted to characterize the properties of elastomers and the development of hyperelastic and viscoelastic models will be presented.

2.1 Experimental investigations

The experiments in the literature mainly focus on revealing the representative hyperelastic and viscoelastic behaviors of elastomers, validating constitutive models and exploring the effects of the microstructure on the characteristics of elastomers.

Series of standard tests, including uniaxial tension test, biaxial tension test, cyclic loading-unloading tests, pure shear test, and stress relaxation test, are often preformed to obtain the stress-stretch response curves of certain elastomers. In addition to reflecting the hyperelastic and viscoelastic behavior of elastomers quantitatively, the obtained experimental data are further used to validate constitutive models and identify the corresponding material parameters through data fitting. Gerke [43] proposed an oscillation method to obtain equilibrium stress-strain curves of vulcanized rubber, which were further used to validate the constitutive model proposed by Mooney [44]. One of the most well-known experiments in the literature was performed on vulcanized rubber by Treloar [45] including uniaxial elongation, equibiaxial tension, pure shear, and uniaxial elongation combined with shear in the same plane. Treloar’s data offered validation to the statistical theory of rubber elasticity proposed by Wall [25], which assumed the uniform length of chain segments in a 3-dimensional polymer network and gave an expression of the strain energy density function to the molecular-network model. Compared with Treloar’s data, the theoretical relations derived from the molecular-network model are in good agreement.
with the experimental data from the biaxial tension test, but less satisfactory for the uniaxial tension and pure shear tests. These data were further used to validate a variety of constitutive models, including Mooney-Rivlin model [21, 44], neo-Hookean model [21, 25, 46] and Ogden model [22]. Tests conducted by Rivlin and Saunders [47] were to obtain load-deformation curves under different types of deformations for vulcanized rubber specimen, showing that the load-deformation characteristics of some simple types of deformations can be explained in terms of a single form of the strain energy density function $W$ (the generalized Rivlin model). Arruda and Boyce [29] carried out uniaxial compression test and plain-strain compression test on three types of rubbers, including silicone rubber, neoprene rubber and gum rubber. The obtained stress-strain curves were used for data-fitting with the 8-chain model they developed. Bergstrom and Boyce [36] obtained the material response of carbon black-filled rubbers that were subjected to different time-history loading conditions. Based on these experimental data, they developed a new micromechanism inspired constitutive model, which is able to provide good quantitative agreement with the experimental response under different strain rates and relaxations. Miehe and Goketepe [38] conducted monotonic and cyclic loading tests and relaxation tests on highly saturated nitrile rubber HNBR50 under uniaxial deformation to assess their non-affine micro-sphere constitutive model [38]. Hossain et al. [48] quantified the mechanical properties of dielectric elastomers VHB 4910 by fitting constitutive relations to experimental data from cyclic loading-unloading tests and relaxation tests. Wang et al. [49] also performed uniaxial tension test on VHB 4910. Unlike Hossain et al. [48], instead of using the stress after long period of relaxation as the data of quasi-static condition, Wang et al. [49] obtained the quasi-static stress-stretch curve for VHB 4910 under an extremely low stretch rate. A common response behavior of elastomers, i.e., Mullins’ effect [50], was also observed in the experiments. This effect is a stress-softening behavior that is characterized by a lower resulting stress in response to the same applied stretch in the successive loading-unloading cycles. Lion [34] performed cyclic loading-unloading processes at different strain rates with relaxation intervals on carbon black-filled rubber, separating the Mullins’ softening effect from other viscoelastic behaviors such as rate-dependent behavior and hysteresis. These experimental data were fitted well with the prediction of the constitutive model developed by Lion [34]. Dorfmann
and Ogden [51] carried out a series of cyclic loading–unloading uniaxial extension tests on the particle-reinforced rubbers to assess the Mullins’ effect and the accumulated residual strain in the unloading paths. They also developed a constitutive model to describe such effects, demonstrating a satisfactory fit with the corresponding experimental data. Diani et al. [52] also performed loading–unloading uniaxial extension tests on the carbon-black-filled sulfur-vulcanized rubber to evaluate the overall properties of the Mullins’ effect, including strain softening, crystallization, permanent set, induced anisotropy, and recovery.

The comparison between the experimental data and the predictions from both phenomenological models and physically motivated models concludes that all these models have limited capability in characterizing the overall properties of the Mullins’ effect.

Moreover, some experiments also attempt to interpret the material behaviors of elastomers from the microscopic perspective. For example, Straube et al. [53] used the small-angle neutron scattering method to investigate the influence of topological tube constraints on the microscopic deformation of the network chains in a rubber under uniaxial deformation, showing evidence to the assumption that the diameter of the tube providing topological constraint varies with the macroscopic deformation according to the tube model [54-55]. Suzuki et al. [56] explored the electron spin resonance technique to measure the chain scission in order to evaluate the impact of the bond rupture [57] on the Mullins’ effect of the filled and unfilled SBR. Ott et al. [58] used proton multiple-quantum nuclear magnetic resonance (NMR) technique to investigate the correlation between the macroscopic deformation and the effects of the chain deformation and orientation for the moderately to highly crosslinked vulcanized rubbers. They also provided a comprehensive comparison of the experimental data with the predictions from various constitutive models, including the affine fixed-junction model, the phantom model, and different tube model variants. It is concluded from this work that none of these models has the capability of describing the entire measured local properties.

These standard experiments can be conducted to provide useful data to assess the capability of material constitutive models in describing the viscoelastic behavior of elastomers under finite deformation. In order to characterize the material properties of any elastomeric
material, we can use the response curves from these standard tests for data-fitting to select the appropriate constitutive models and identify the corresponding material property parameters, which is the focus of this thesis work.

2.2 Hyperelastic constitutive models

Due to hyperelasticity, elastomers exhibit a nonlinear stress-stretch response when subjected to large deformation, which cannot be described adequately by the theory of linear elasticity. To accurately understand such nonlinear behavior exhibited by elastomeric materials, various hyperelastic constitutive models have been developed to describe the nonlinear elasticity. The development of the theory of nonlinear elasticity is outlined in detail in the works of Ogden [59] and Holzapfel [60]. In the literature, the hyperelastic constitutive models are generally classified into two categories. One category includes the phenomenological models established on the basis of continuum mechanics framework, the other is based on statistical mechanics treatment linking the macroscopic behavior of elastomeric materials to their microstructure [61-63]. However, it should be mentioned that the distinction between these two types of models is not clear sometimes as certain phenomenological models also attempt to involve the physics nature of materials. The kernel of these models is the definition of strain energy density function.

The strain energy density function of the phenomenological models is defined either in terms of strain invariants or principal stretches, from which the nonlinear stress-strain relation can be derived accordingly for Green elastic material [64]. One of the examples is the generalized Rivlin model [47], which is also called polynomial hyperelastic model with the strain energy density function being expressed in terms of three strain invariants. Since most elastomeric materials are considered as incompressible [65], the strain energy density function of the generalized Rivlin model is simplified as a function of the first two invariants $I_1$ and $I_2$ of the left Cauchy-Green deformation tensor, i.e.,

$$W_R(I_1, I_2) = \sum_{i=0, j=0}^M C_{ij} (I_1 - 3)^i (I_2 - 3)^j$$

with $C_{ij}$ being the material constants related to the shear modulus and $C_{00} = 0$. The Mooney-Rivlin model [21, 44] is a special case of the generalized Rivlin model when $M=1$ and $C_{11} = 0$. Particularly when $C_{01} = 0$, the Mooney-
Rivlin model is reduced to the neo-Hookean model [21, 25, 46], in which only the first invariant is accounted. Another special case is when \( j = 0 \) while \( i \) takes 1, 2 and 3 respectively, the generalized Rivlin model is reduced to the Yeoh model [23] to include the effect of the higher order of the first invariant \( I_i \). In reality, polymer network has a limit to the extension of polymer chains. However, none of the models mentioned above take the extensibility limit of polymer chains into account. Gent [24] proposed a model to account for such extensibility of polymer chains. For the limiting case, the Gent model will be reduced to the neo-Hookean model.

Some phenomenological models are also developed in terms of the principal stretches. Vanlanis and Landel [66] made an assumption that the strain energy density function could be written as a sum of independent functions of the three principal stretches, i.e.,

\[
W_{VL} = w(\lambda_1) + w(\lambda_2) + w(\lambda_3),
\]

where \( w(\lambda_i) \) takes the same format with respect to each stretch component [66-67]. The Ogden model [22] is a special case of the Vanlanis-Landel model, i.e.,

\[
w(\lambda_i) = \sum_{k=1}^{K} \frac{\mu_k}{\alpha_k} \left( \lambda_i^{\alpha_k} - 1 \right), i = 1, 2, 3
\]

with \( \mu_k \) and \( \alpha_k \) being material constants related to the shear modulus, which are interpreted by Ehret [68] from the molecular-statistical basis. Although the models based on the Vanlanis-Landel assumption are accurate to predict the response behavior of rubber-like materials over a large range of deformation, there exists a restriction for the separable form of \( w(\lambda_i) \) in the Vanlanis-Landel model since not all the strain energy density functions of constitutive models can be expressed as a separable function of the individual principal stretch [69]. The necessary and sufficient conditions of the invariant-based strain energy density functions to be expressed in the Vanlanis-Landel format were further commented by Rivlin and Sawyers [69]. As argued by Zhou et al. [42], all those phenomenological models are only sufficient to characterize the empirical stress-strain relations but lack the physical interpretations for the involved material parameters. This issue has been tackled by researchers to revisit these models, attempting to reveal the physical foundation of those models from the molecular-statistical perspective. For example, Fried [70] analyzed the Mooney [44] and Rivlin–Saunders [47] theories of rubber elasticity from the molecular-statistical perspective that the macroscopic deformation is linked to the end-to-end vectors of molecules. It was found
that different manners of the transformation of the end-to-end vectors under a macroscopic deformation led to different forms of strain energy densities for the neo-Hookean model, the Mooney-Rivlin model, and the Rivlin-Saunders model. Horgan and Saccomandi [71] compared the Gent model and other models obtained from molecular arguments using the non-Gaussian probability distribution function [26], concluding that the Gent model provided a good approximation of such models. They also provided correlation between the coefficients in the Gent model and the related microscopic quantities.

Alternatively, the constitutive models stemming from the statistical mechanics treatment have also been developed to predict the hyperelastic behavior of elastomers. From the molecular-statistical perspective, a rubber-like material is idealized as consisting of a number of polymer chains cross-linked at certain junction-points [72]. The polymer chains are described by the parameters of polymer physics and chemistry, including the chemical composition, the cross-linking density, the molecular weight of monomers, the chain extensibility, the polymerization degree and the amount of polymer chain entanglements to reflect the microstructure of the material [42]. As the statistical mechanics treatment takes the features of microstructure into account, these constitutive models can thus connect the macroscopic response of the elastomers to the material microstructure directly. Wall [25] made an assumption that the length of all segments of any chains between two junction-points is identical. Based on this assumption, Wall [25] and Treloar [46] obtained the strain energy density function, which is in the equivalent format of the neo-Hookean model while bestows the material parameter in the neo-Hookean model [21] with physical justification. Since the Gaussian approximation is involved in describing the distribution of polymer chains, these models are also called the Gaussian network models. However, the Gaussian approximation is only valid when the length of polymer chains is significantly less than its extensibility limit, meaning that the Gaussian network models are only applicable when the polymer chains are not fully extended [25]. To model the stress-stretch behavior when the polymer chains are approaching their maximum extension, the non-Gaussian network models are thus developed, including the 3-chain model [27, 73], the 4-chain model [28] and the 8-chain model [29]. The distribution of polymer chains in these non-Gaussian network models follows the Kuhn–Grün probability distribution function [26], which is the first order approximation of the Rayleigh’s exact Fourier integral
representation [73]. The main difference between these chain models is that the current length of the end-to-end chain vector with finite extensibility is defined in different chain cell structures as discussed by Beatty [74].

It should be mentioned that both the Gaussian and the non-Gaussian network models adhere the affinity of network deformation to the macroscopic deformation. Therefore, those affine models fail to represent the real molecular structure of elastomers as they are not capable of fully capturing the entanglement effect of polymer chains. As addressed in the literature, the entanglement effect was modeled as topological constraints on the polymer chains, which was further interpreted by several non-affine constitutive models. In the Edwards’s tube model [75], the topological entanglement is applied to each monomer of polymer chains, implying that the fluctuations of polymer chains are restricted in a confined tube. In the constrained-junction model [76-78], the entanglement effect is modeled as topological constraints acting on the junction points of the crosslinked polymer chains to confine the network fluctuations. In the slip-link model [79-80], the entanglement is modeled as slip-links connecting neighboring polymer chains, which are allowed to slide along the contour of the two chains up to a fixed distance. The entanglement in the slip-link model restricts the entire contour of chains. Vilgis and Erman [81] compared the constrained-junction model and the slip-link model and summarized the similarities and differences of these two models. Rubinstein and Panyukov [82] combined the features of the confined tube model and the slip-link model to establish a new slip-tube model, which provides prediction in good agreement with the uniaxial experimental data of some rubbers. These models are also able to characterize the strain softening behavior due to the account of the effect of the chain entanglement. However, these models cannot capture the strain hardening behavior of elastomers under large deformation. In order to tackle this issue, Davidson and Goulbourne [30] developed their non-affine model by combining the concepts of the slip-tube model [82] and the 8-chain model [29], which is capable of characterizing the effect of both the crosslinked polymer network and the entanglement of polymer chains for elastomers under finite deformation. The material parameters in this non-affine model are associated with the crosslinked network, the chain entanglement as well as the extensibility of the polymer networks. The non-affine micro-sphere model proposed by Miehe et al. [37] defines the micro-mechanical response of a single polymer
chain in a constrained environment on a micro-sphere orientation, and uses a micro to macro transition to link the defined micro-kinetic variables to the macroscopic variables, but two micro-macro averaging parameters of this model lack of a physical interpretation.

### 2.3 Viscoelastic models

Viscoelasticity is an intrinsic nature of most elastomeric materials. The viscoelastic response of elastomers is mainly characterized by the stress relaxation tests and the creep strain tests, and parameters related to viscoelasticity can be determined by data fitting with experimental results. Extensive constitutive models have been developed to describe the viscoelastic behavior. Viscoelastic relations may be described in either integral or differential format. The integral form is a general representation of the nature of viscoelasticity and is more suitable for theoretical studies [83], while the differential form derived from rheological models can provide a more direct physical interpretation of the viscoelastic behavior [84]. In this section, the development of rheological models and viscoelastic constitutive models will be discussed.

#### 2.3.1 Rheological models

Instead of dealing with the real complex polymer chains in an elastomer, rheological models are developed to describe the viscoelastic behavior by mechanical analogies. During the deformation of a viscoelastic material, part of the total work of deformation is dissipated due to the material viscosity while the remaining energy is stored elastically [85]. Therefore, the mechanical analogies consist of an elastic component represented by a spring element and a viscous component represented by a dashpot element as shown in Figure 2-1 [83]. The spring element follows the Hooke’s law to describe the relation between the stress $\sigma$ and the strain $\varepsilon$, i.e.,

$$\sigma(t) = \mu \varepsilon(t) \quad (2.1)$$

where $\mu$ is the modulus of the elasticity. The dashpot element obeys the Newtonian law of viscosity that the stress $\sigma$ is proportional to the rate of strain $\dot{\varepsilon}$, i.e.,
\[ \sigma(t) = \eta \dot{\varepsilon}(t) \] (2.2)

where \( \eta \) is the viscosity, and the strain rate \( \dot{\varepsilon} \) is defined as \( \dot{\varepsilon}(t) = \partial \varepsilon / \partial t \).

Various arrangements of the Hookean spring and the Newtonian dashpot construct different rheological models. The Maxwell model [83] is a combination of the spring element and the dashpot element in series as shown in Figure 2-2. The stress \( \sigma \) acting on the spring and the dashpot is the same while the total strain \( \varepsilon \) is the summation of the strain \( \varepsilon_c \) of the spring element and the strain \( \varepsilon_v \) of the dashpot element. This model is capable of describing the stresses relaxation under a constant strain, while it fails to capture the viscoelastic creep. When the Hookean spring and the Newtonian dashpot are arranged in parallel, it results in the Kelvin-Voigt model [83], in which the strain of the spring and the dashpot is the same \( (\varepsilon = \varepsilon_c = \varepsilon_v) \), while the total stress is the summation of the stress of these two elements \( (\sigma = \sigma_c + \sigma_v) \). This model can accurately predict the creep scenario under a constant stress, while fails to capture the relaxation behavior.

---

**Figure 2-1 The spring and dashpot element**
The Maxwell and Kelvin-Voigt models are widely used in the conceptual analysis to describe the linear viscoelastic behavior. Tobolsky and Andrew [86] pointed out that a single Maxwell or a single Kelvin-Voigt model may not be enough to characterize the behavior of polymers. It could be more accurate to use more than one element in parallel or in series to model the material behavior due to the various types of diffusive polymer chains. The generalized models assign Maxwell elements in parallel with a ground spring element or arrange Kelvin-Voigt elements in series with a ground spring element, which are depicted in Figure 2-4. The ground spring element represents the pure elastic ground network, while the parallel Maxwell elements and the Kelvin-Voigt elements in series represent different viscoelastic subnetworks. The generalized Maxwell model is also called the parallel rheological model. For the generalized rheology models, the total strain energy...
density $W_i$ consists of two parts, one part ($W^e$) stored in the spring of the elastic ground network and the other part ($W^v_n$) stored in the spring element of the individual viscoelastic subnetwork, i.e. $W_i = W^e + \sum_{n=1}^{N} W^v_n$ with $N$ being the total number of the viscoelastic subnetworks.

![Figure 2-4 Generalized rheological models. (a) generalized Maxwell model; (b) generalized Kelvin-Voigt model](image)

### 2.3.2 Viscoelastic constitutive models

The development of the linear viscoelasticity theory can be dated back to the work by Green and Tobolsky [87], in which the kinetic theory of elasticity [27, 88] was extended with a relaxation hypothesis stating that the formation and breakage of bonds between molecules cause the decay of stress during the relaxation. Incorporating this assumption, they used linear differential equations of internal strain-like variables as the evolution equation to describe the internal strain of polymer chains. Based on this linear viscoelastic theory, Lubliner [31] split the free energy of a viscoelastic material into a rate-dependent part and a time-dependent part. In this work, the internal strain-like variables were interpreted as the inelastic stains and the multiplicative decomposition scheme of the deformation gradient was postulated to decompose the deformation gradient into an elastic part and an inelastic part. The multiplicative decomposition of the deformation gradient was originally suggested by Lee [89] to describe the elastoplastic deformation. Following the same multiplicative decomposition scheme, the viscoelastic constitutive models by Sidoroff [90] and Reese and Govindjee [91] were developed based on the thermodynamics
Some viscoelastic constitutive models have also been developed based on alternative selection of the internal strain-like variables. For example, Simo [32] proposed a finite-stain theory of viscoelasticity and developed a three-dimensional damage model to describe the combined viscoelastic behavior of the rate dependence and the Mullins’ effect, which is based on the thermodynamics evolution law in terms of the inelastic stress, known as overstress (as an alternative internal variable). Based on the model proposed by Simo [32], Lion [34] developed a viscoelastic model for carbon black-filled rubber to capture both the Mullins’ effect and the nonlinear rate-dependent viscoelastic behavior. The nonlinear rate dependence was described by decomposing the total stress into an equilibrium stress and a rate-dependent overstress as dual internal variables. The prediction results of Lion's model have an excellent agreement with the experimental data [34].

The viscoelastic constitutive models mentioned above are all phenomenological models, which are able to qualitatively predict certain viscoelastic behavior of elastomers. However, they lack the interpretation on the physical mechanisms of the viscoelasticity as the microstructure features are not reflected by the material parameters in those models. To tackle such a limitation, the theories of polymer dynamics are introduced for the development of viscoelastic constitutive models. One example is the tube model [54, 55], which assumed that the motion of polymer chains is confined in a tube-like region by topological constraints. When the elastomer is under deformation, the elastic stress is sustained by the cross-linked ground network, while the inelastic stress is attributed to the reptation of polymer chains confined by the tube. Based on the concept of such a tube model, some micromechanism inspired constitutive models have been developed by researchers in the literature [36, 38, 39]. Despite that some internal variables in these models lack physical justification, they still predict the response of elastomers in good agreement with experimental data [36, 38-39]. Nevertheless, one limitation of these models is the adoption of constant material viscosity during the relaxation process, which contradicted with some experimental observations, i.e., material viscosity is deformation-dependent [53, 58, 92]. It is a more realistic situation particularly when the elastomer is undergoing large deformation, which could also be justified by the tube model from a physical perspective. The length and diameter of the tube vary with the deformation of the elastomers, which will thus change the topological constraints on the reptation of the
polymer chain within the tube and its relaxation process, leading to a deformation-dependent viscosity. With this consideration, Tang et al. [40] and Li et al. [11, 12, 41] have proposed micro-mechanically based constitutive models to characterize the nonlinear viscoelastic behavior of both vulcanized and un-vulcanized natural rubbers. To take the advantage of the complementary merits of the micromechanism inspired models and the micro-mechanically based models, Zhou et al. [42] developed a new micro-macro constitutive model to capture the viscoelastic response of elastomers under finite deformation, which allows the adoption of most of the hyperelastic constitutive models and easy implementation in the finite element analysis. In this model, all the material parameters have a microscopic foundation or a microstructural justification.
3 Material Property Characterization of Elastomers

This section presents the detailed steps of developing the material property characterization package. First, the continuum mechanics framework of the material property characterization package is outlined. The mathematical treatment on the nonlinear viscosity is further introduced. These two parts constitute the theoretical foundation of the material property characterization package. Then, the stress responses of elastomers under uniaxial loading condition are formulated according to six hyperelastic constitutive models, which will be used to establish the constitutive model database. Finally, the corresponding selection strategy is explained.

3.1 Continuum mechanics framework

The continuum mechanics modeling framework on the viscoelastic behavior of elastomeric materials is based on the pioneering works of Bergström and Boyce [36], Sidoroff [90], and Reese and Govindjee [91]. Elastomers are assumed to comprise idealized polymer networks as shown in Figure 3-1, i.e., an elastic ground network formed by cross-linked polymer chains and some subnetworks formed by different types of diffusive polymer chains. In general, elastomers are characterized as hyperelastic and viscous materials. The hyperelasticity of elastomers originates from the strong and flexible cross-linked ground network, leading to large deformation sustainability and nonlinear stress-strain behavior. On the other hand, the material viscosity mainly attributes to the reptation of polymer chains, demonstrating time-dependent and rate-dependent response behaviors. Such hyperelastic and viscous behavior of elastomers are commonly described by the
parallel rheological model in the finite-deformation viscoelasticity theory [93], schematically shown in Figure 3-2. Two different types of polymer chains are captured by this parallel rheological model, in which network A is the purely elastic network formed by the cross-linked polymer chains, while subnetworks \( B_n \) \((n=1, 2…N)\) are formed by free chains and relax with time and dissipate energy. The existence of multiple subnetworks is due to the fact that free chains may have different diffusion capability. The common practice in using this rheological model is to describe the viscoelastic behavior of elastomers by multiplicatively decomposing the deformation into two parts, namely, an elastic part and an inelastic part (viscous part), as depicted hereinafter by the superscript “\( e \)” and “\( i \)”, respectively.
Consider a reference configuration (undeformed and stress-free) $\Omega_0$ of an elastomer, the material point described by the position vector $X$ in $\Omega_0$ moves to the current position $x(X, t)$ in the current configuration $\Omega$ after deformation, as shown in Figure 3-3. The components of the deformation gradient tensor $F(X, t)$ are defined as $F_{iK} = \frac{\partial x_i}{\partial X_K}$. For elastomers, they may not be in the thermodynamic equilibrium state most of the time due to their viscoelastic properties. To describe the viscoelastic deformation of the elastomers, we follow the common approach adopted in the finite-deformation viscoelasticity and plasticity [89, 91, 93], in which an imaginary intermediate state is introduced between the reference state $\Omega_0$ and the current state $\Omega$ as demonstrated in Figure 3-3. This imaginary state can be achieved by relaxing the elastomer in the current state $\Omega$. Therefore, the material is fully relaxed in the imaginary state. Here we define the deformation gradient of the current state $\Omega$ with respect to the imaginary state as $F^e(X, t)$, and the deformation gradient of the imaginary state with respect to the reference state $\Omega_0$ as $F^i(X, t)$, which is irreversible. $F^e(X, t)$ is related to the elastic deformation, while $F^i(X, t)$ is related to the inelastic deformation. Thus, the arbitrary deformation gradient $F$ is multiplicatively decomposed into two parts as $F = F^e F^i$. Therefore, for each subnetwork in the parallel rheological model in Figure 3-2, the multiplicative decomposition on the deformation gradient results in $F_{B_n} = F^e_{B_n} F^i_{B_n}$. $F^e_{B_n}$ represents the elastic deformation of the spring and $F^i_{B_n}$ stands for the inelastic deformation of the piston in each subnetwork. It should be noted that as the deformation acts on all the polymer networks, $F = F_A = F_{B_n}$, $(n=1, 2, \ldots, N)$ always holds true in the parallel rheological model as shown in Figure 3-2.
Following Reese and Govindjee [91], the total Helmholtz free energy density of the current system is split into two parts, i.e., the equilibrium Helmholtz free energy density $W^{EQ}$ stored in the spring of the ground network A and the non-equilibrium Helmholtz free energy density $W^{NEQ}$ stored in the Maxwell elements representing the diffusive polymer chains, as

$$
W\left(F_A, F^e_{B_1}, F^e_{B_2}, \ldots, F^e_{B_N}\right) = W^{EQ} + W^{NEQ} = W_A\left(F_A\right) + \sum_{n=1}^{N} W_{B_n}\left(F^e_{B_n}\right)
$$

(3.1)

where $W_A\left(F_A\right)$ represents the energy stored in the ground network A and $W_{B_n}\left(F^e_{B_n}\right)$ is the energy stored in the spring of each Maxwell element $B_n$. In the thermodynamic equilibrium state, the spring of each Maxwell element is fully relaxed ($F^e_{B_n} = 0$), resulting in $W^{NEQ} = 0$. Correspondingly, the total energy consists only of the equilibrium part $W^{EQ}$ when the system is in a thermodynamic equilibrium state.

Following the argument of Coleman and Gurtin [92], even when the system is in a non-equilibrium state, the first Piola-Kirchhoff stress (the transpose of the nominal stress) is defined as,

$$
P = \frac{\partial W}{\partial \mathbf{F}} = \frac{\partial W_A\left(F_A\right)}{\partial \mathbf{F}} + \sum_{n=1}^{N} \frac{\partial W_{B_n}\left(F^e_{B_n}\right)}{\partial \mathbf{F}}
$$

(3.2)
where \( F_{B_B}^i = F_{B_B} \left( F_{B_B}^i \right)^{-1} \). As large deformation is usually expected in correspondence to the soft nature of the material, there exists large discrepancy between the nominal fields and the true fields. It is necessary to provide the expression for the true field quantities. According to the relation between the Cauchy stress (true stress) \( \sigma \) and the first Piola-Kirchhoff stress \( P \), i.e., \( P = J\sigma F^{-T} \) with \( J = \det(F) \), the Cauchy stress is thus expressed as,

\[
\sigma = J^{-1} \frac{\partial W}{\partial F} F^T = J^{-1} \frac{\partial W_A}{\partial F} (F_A)^T + \sum_{n=1}^{N} J^{-1} \frac{\partial W_{B_n}}{\partial F} \left[ F_{B_n} \left( F_{B_n}^i \right)^{-1} \right] F^T
\]  

(3.3)

Consider a deformable elastomer body occupying a volume \( V \) with surface \( S \) as shown in Figure 3-4, which is mechanically loaded with a body force \( b_i(X, t) \) and a surface traction \( t_i(X, t) \). The application of the mechanical loads results in a field of displacement of the material particle \( X_i \) in the reference state to the current state with the position vector \( x_i(X, t) \). The first Piola-Kirchhoff stress is also defined as the work conjugate to the deformation gradient [93], i.e.,

\[
\int_V P_{ik} \frac{\partial x_i}{\partial x_k} dV = \int_V b_i x_i dV + \int_S t_i x_i dA
\]  

(3.4)

which states that the mechanical work done by external forces over any admissible displacement field always equals the work done by stress over the corresponding field of deformation gradient, regardless of thermodynamic state. The linear momentum conservation for this system results in the force balance equation for the material point in the elastomer body as,

\[
\frac{\partial P_{ik}}{\partial x_k} + b_i = 0
\]  

(3.5)

It is the mathematically equivalent definition of the first Piola–Kirchhoff stress [93], which can be obtained by employing the convergence theorem on the left-hand side of Eq. (3.4). This will also result in the following boundary condition on the surface of the elastomer body in terms of the Piola-Kirchhoff stress, i.e.,
\[(P^+_{ik} - P^-_{ik}) n_K = t_i \quad (3.6)\]

where ‘\(\text{+}\)’ and ‘\(-\)’ indicates the outward and the inward direction of the medium, respectively; the unit vector \(n_K\) is normal to the surface in the reference state, pointing outwards the medium.

According to a small change on the deformation, the change of the free energy of the system can be expressed in terms of the Helmholtz energy density \(W\) and the work done by the external forces, as,

\[
\delta G = \int_V \delta W dV - \int_V b_i \delta x_i dV - \int_S t_i \delta x_i dS \quad (3.7)
\]

Substituting Eq. (3.4) into Eq. (3.7) results in,

\[
\delta G = \int \left( \delta W - P : \delta F \right) dV \quad (3.8)
\]

The law of thermodynamics dictates that the free energy of a material system never increases under an isothermal condition, i.e.,

\[
\delta G \leq 0 \quad (3.9)
\]
As inequality in Eq. (3.9) holds true on any material particle during any process, therefore, we have,

\[ \partial W - \mathbf{P} : \partial \mathbf{F} \leq 0 \]  \hspace{1cm} (3.10)

The equal sign takes place only when the system is locally in equilibrium. Particularly, considering that the elastomer is in a thermodynamic equilibrium state, we can obtain \( W = W^{\text{EQ}}(\mathbf{F}) \) from Eq. (3.1), and

\[ \delta W^{\text{EQ}} = \mathbf{p}^{\text{EQ}} : \delta \mathbf{F} \]  \hspace{1cm} (3.11)

Then the first Piola-Kirchhoff stress in the equilibrium state is determined as,

\[ \mathbf{p}^{\text{EQ}} = \frac{\partial W^{\text{EQ}}(\mathbf{F})}{\partial \mathbf{F}} \]  \hspace{1cm} (3.12)

For the non-equilibrium state, substituting Eq. (3.1) into Eq. (3.10), we can have,

\[ \left( \mathbf{P} - \partial W \right) : \delta \mathbf{F} - \sum_{n=1}^{N} \partial W_{\mathbf{F}^{i}_{n}}^{\text{NEQ}} \frac{\partial \mathbf{F}_{\mathbf{F}^{i}_{n}}}{\partial \mathbf{F}^{i}_{n}} : \delta \mathbf{F}^{i}_{n} \leq 0 \]  \hspace{1cm} (3.13)

From the definition of the first Piola-Kirchhoff stress in Eq. (3.2), only the second term in the inequality (3.13) retains, i.e.,

\[ \sum_{n=1}^{N} \mathbf{P}^{\text{NEQ}}_{\mathbf{F}^{i}_{n}} : \mathbf{F}_{\mathbf{F}^{i}_{n}} \left( \mathbf{F}_{\mathbf{F}^{i}_{n}} \right)^{-1} \delta \mathbf{F}^{i}_{n} \geq 0 \]  \hspace{1cm} (3.14)

Meanwhile, the first Piola-Kirchhoff stress is expressed as,

\[ \mathbf{P} = \mathbf{p}^{\text{EQ}} + \sum_{n=1}^{N} \mathbf{P}^{\text{NEQ}}_{\mathbf{F}^{i}_{n}} \left( \mathbf{F}_{\mathbf{F}^{i}_{n}} \right)^{-1} \]  \hspace{1cm} (3.15)

where the inelastic first Piola-Kirchhoff stress tensor \( \mathbf{P}^{\text{NEQ}}_{\mathbf{F}^{i}_{n}} \) is defined as
\[
\begin{align*}
\mathbf{P}^{\text{NEQ}}_{B_v} &= \frac{\partial W^{\text{NEQ}}_{B_v} (\mathbf{F}^e_{B_v})}{\partial \mathbf{F}^e_{B_v}} \quad (3.16)
\end{align*}
\]

Similarly, the inelastic Cauchy stress is defined as,

\[
\sigma^{\text{NEQ}}_{B_v} = \frac{\mathbf{P}^{\text{NEQ}}_{B_v} (\mathbf{F}^e_{B_v})^T}{\det (\mathbf{F}^e_{B_v})} \quad (3.17)
\]

Due to the rate-dependent behavior of the viscoelastic elastomers, it is a common practice to replace the variation expressions by their corresponding rate of change, i.e., \( \partial \mathbf{F}^i / \partial t \) or \( \dot{\mathbf{F}}^i \) (Hong, 2011; Zhou et al., 2018). Thus, the inequality (3.14) is re-written as,

\[
\sigma^{\text{NEQ}}_{B_v} : \mathbf{L}^i \geq 0 \quad (3.18)
\]

where \( \mathbf{L}^i = \dot{\mathbf{F}}^i (\mathbf{F}^i)^{-1} \) is the inelastic part of the covariant velocity gradient,

\[
\begin{align*}
L_{ij} &= \dot{F}_{ik}^L H_{kj} = L_{ij}^L + L_{ij}^H = F_{im}^e H_{mj}^e + F_{im}^e \dot{F}_{jk}^i H_{pj}^e + F_{im}^e \dot{F}_{jk}^i H_{pj}^e \\
&= (1) + (2) + (3)
\end{align*}
\]

with \( \mathbf{H} = \mathbf{F}^{-1} \). Due to the symmetricity of the Cauchy stress tensor, the inequality (3.18) can also be written as,

\[
\sigma^{\text{NEQ}}_{B_v} : \mathbf{D}^i \geq 0 \quad (3.20)
\]

where \( \mathbf{D}^i \) is the symmetric part of the inelastic velocity gradient, i.e., the so-called inelastic stretch rate tensor with \( \mathbf{D}^i = \frac{1}{2} \left[ \mathbf{L}^i + (\mathbf{L}^i)^T \right] \).

To make inequality (3.20) always hold true at any process for all materials, a kinetic evolution law,

\[
\mathbf{D}^i = \mathbf{M} : \sigma^{\text{NEQ}} \quad (3.21)
\]
is often used in practice [91, 94], in which $\mathbf{M}$ is definitely positive to ensure the inequality (3.20) is automatically satisfied. In the work of Reese and Govindjee [91], for the incompressible elastomers, the material-dependent fourth-rank mobility tensor is defined as,

$$
\mathbf{M} = \frac{1}{2\eta_{b_n}} \left( \mathbf{I}^4 - \frac{1}{3} \mathbf{I} \otimes \mathbf{I} \right)
$$

(3.22)

where $\eta_{b_n}$ is the viscosity of the viscous subnetwork $B_n$, $\mathbf{I}^4$ is the 4th-order symmetric identity tensor, and $\mathbf{I}$ is the 2nd-order identity tensor.

### 3.2 Nonlinear material viscosity

In order to implement the kinetic evolution law Eq. (3.21) to determine the inelastic deformation of the elastomers, the material viscosity $\eta_{b_n}$ needs to be constitutively prescribed for each subnetwork in the parallel rheological model. For most existing works in the literature, the viscosity $\eta_{b_n}$ is often assumed as a constant for simplicity purpose in modeling the viscoelastic behavior of elastomers. This assumption is valid only when the material is subjected to small deformation. However, the material viscosity was observed to vary with the deformation of elastomers in experiments [53, 58, 95], particularly when the material undergoes finite deformation. To tackle this issue, Zhou et al. [42] proposed a micro-macro constitutive model for finite-deformation viscoelasticity of elastomers based on the well-known tube model and the theory of polymer dynamics [54-55]. In this model, all material parameters have a microscopic foundation or a microstructural justification. Meanwhile, the deformation-dependent material viscosity is incorporated into the continuum finite-deformation viscoelasticity theory. Here we will elaborate this constitutive model, as it is the basis of the modeling framework of this thesis, along with parallel rheological model.

Elastomeric materials comprise many polymer chains. The material viscosity is considered to originate from the diffusion of polymer chains, which is described by the tube model [55]. One typical polymer chain A-B in an elastomer is schematically plotted in Figure 3-5.
which could be either cross-linked or entangled with other polymer chains nearby. Figure 3-5(a) illustrates the cross-linked strand A-B, while Figure 3-5(b) illustrates the entangled one. In this figure, the polymer chain is placed on a plane with the dots representing the cross-sections of the other strands. Due to the topological constraints, the strand A-B cannot cross the dots, i.e., the other polymer chains perpendicular to the plane it occupies. Therefore, it is naturally believed that the number of conformations allowed for the chain A-B is much less than that in the free space. Considering the constraint from the surrounding polymer chains, this polymer chain A-B is assumed to be confined in a tube-like region with diameter of \( a \) as represented by the dashed line in this figure. The axis of the tube, which represents the shortest path connecting the two ends of the strand with the same topology as the polymer chain itself relative to the surrounding obstacles, is defined as the primitive chain of the strand A-B. It means that the conformations which go outside the tube are likely to violate the topological constraints. This assumption of the fixed tube is valid for the elastomers with a highly concentrated state of long chains. As for this case, it is unlikely for the tube to fluctuate because such fluctuation involves the distortion of many other polymer chains.

The variation of the material viscosity with the macroscopic deformation of the elastomer can be justified by the diffusion of the polymer chain confined in this tube from a physical perspective. Such a diffusion process of the polymer chain is characterized based on time scale as argued by Zhou et al. [42]. In the short-time scale, the polymer chain wriggles around the primitive chain within the tube, which can be represented by the Brownian
motion. While in the long-time scale, the polymer chain starts to reptate along the tube and disengages from the original tube, creating and destroying the ends of the primitive chain as shown in Figure 3-6 [42]. Particularly when the elastomer undergoes large deformation, the length and diameter of the tube could be significantly changed, affecting the reptation ability of the polymer chain. Consequently, the material viscosity varies with the macroscopic deformation of the elastomer.

As proposed by Doi and Edwards [54], the viscosity of a viscous subnetwork in polymer is expressed in terms of the shear relaxation modulus $G_n(t)$, as

$$\eta_{B_n} = \int_0^\infty G_n(t)dt$$  \hspace{1cm} (3.23)

After deformation, the whole polymer chain is restricted by a deformed tube. As time passes, the polymer chain starts to reptate. At an instant $t$, the parts of the polymer chain
near the ends have disengaged from the deformed tube, while the middle part of the chain is still confined in the tube. As only the segment in the deformed tube contributes to the stress, the stress is thus proportional to the fraction $\varphi(t)$ of the polymer chain still confined in deformed tube, i.e.,

$$G_n(t) = G_{n0}\varphi(t)$$

where $G_{n0} = n_{Bn}k_BT\left(\frac{\tau_{s_n}}{\tau_{Rn}}\right)^{1/2}$ is the relaxation modulus (material constant) when the reptation starts; $n_{Bn}$ is the number of polymer chains per unit volume in the viscous subnetwork $B_n$; $k_B$ is the Boltzmann constant; $T$ is the absolute temperature; $\tau_{s_n}$ is the time scale when the polymer chain starts to reptate, associated with the wriggling motion; $\tau_{Rn}$ is the relaxation time of the contour length of the primitive chain [42, 54, 96].

The fraction of the chain confined in the tube at an instant $t$ is defined as [42],

$$\varphi(t) = \frac{1}{L} \int_0^L \int_s^{s+L} \Psi(\xi, t; s) d\xi ds$$

where $\Psi(\xi, t; s)$ is the probability for the primitive chain with moving distance $\xi$ in the tube, while its ends have not reached the segment $s$ of the original tube as shown in Figure 3-7. The probability fulfills the one-dimensional diffusion equation with the expression given by Zhou et al. [42],

$$\Psi(\xi, t; s) = \sum_{p=1}^\infty \frac{2}{L} \sin\left(\frac{p\pi s}{L}\right) \sin\left[\frac{p\pi(s - \xi)}{L}\right] \exp\left(-\frac{p^2 t}{\tau_n^d}\right)$$

with $\tau_n^d$ being the disengagement time of the free chain, which is the time needed to complete the relaxation process [54].

Substituting Eqs. (3.24) - (3.26) to Eq. (3.23), the material viscosity for each subnetwork in the parallel rheological model is calculated as,
\[ \eta_{B_n} = \frac{\pi^2}{12} G_{n0} \tau^d_n \]  

(3.27)

with the disengagement time of the free chain given as,

\[ \tau^d_n = \frac{\zeta N_{B_n}^3 b_0^4}{\pi^2 k_B T \langle a_n^2 \rangle} \]  

(3.28)

where \( a_n \) is the tube diameter after deformation in the current state, \( \zeta \) is the monomer friction constant, \( N_{B_n} \) is the degree of polymerization of chains in the viscous subnetwork \( B_n \), \( b_0 \) is the effective bond length between monomers, and \( \langle * \rangle \) stands for the expectation operation \([42, 54]\). Since the expectation value is also called the average or the mean value in probability and statistics \([97]\), the involved calculation of the expectation value is denoted as the average or mean value hereinafter.

For the case of small deformation, it is reasonable to assume the tube diameter \( a_n \) of and the primitive chain length keep unchanged, which will result in a constant disengagement time \( \tau^d_n \) of the polymer chain and a constant material viscosity \([42]\). However, when the polymer chains undergo finite deformation, these two quantities are assumed to vary with the macroscopic deformation, leading to the nonlinear material viscosity \([42]\). Referring to Figure 3-7, the average of the primitive chain length \( \langle L \rangle \) over all possible initial tangent vector \( u_0 \) and the mean diameter \( \langle a_n \rangle \) of the tube were formulated as \([42]\),

\[ \langle L \rangle = \int \frac{|\mathbf{F} \cdot \mathbf{u}_0|}{4\pi} L_0 d^2 \mathbf{u}_0 \]  

(3.29)

\[ \langle a_n \rangle = \frac{\langle \mathbf{R}_{ee}^2 \rangle}{\langle L \rangle} \]  

(3.30)

where \( L_0 \) is the contour length in the reference state, and the mean square end-to-end distance of the primitive chain \( \langle \mathbf{R}_{ee}^2 \rangle \) was given in the work of Li et al. \([12]\), as
\[ \left\langle R_{ee}^2 \right\rangle = \int |\mathbf{F} \cdot \mathbf{R}|^2 f_0(\mathbf{R}) d^3 \mathbf{R} \]  

(3.31)

with \( f_0(\mathbf{R}) \) being the statistical distribution function of the end-to-end vector \( \mathbf{R} \) of the primitive chain in the reference state. It should be noted here that the primitive chain in the current state is assumed to deform in the same way as the macroscopic deformation [54]. Such an assumption has been verified by molecular dynamic simulations [12]. Correspondingly, the disengagement time \( \tau_n^d \) of the polymer chain in Eq. (3.28) varies with the macroscopic deformation of the elastomer, leading to the nonlinearity of the material viscosity as show in Eq. (3.27).

Figure 3-7 Schematic of a primitive chain in the reference state. The contour length of the primitive chain is \( L_0 \); \( \mathbf{u}_0 \) is the unit tangent vector at contour position \( s \) of the primitive chain; \( \mathbf{R} \) is the end-to-end vector of the primitive chain \[42\].

The deformation-dependent viscosity \( \eta_{Bn} \) of each subnetwork in the parallel rheological model is thus determined as,

\[ \eta_{Bn} = \frac{\eta_{n0}}{\alpha(\mathbf{F})^2} \]  

(3.32)

where \( \eta_{n0} = \frac{\zeta n_B^4 \rho_0^4}{12a_0^2} \left( \frac{\tau_{Rn}}{\tau_{ed}} \right)^{1/2} \) is the viscosity of subnetwork \( B_n \) in the undeformed reference state; \( \alpha(\mathbf{F}) \) is the ratio of mean diameter \( \langle a_s \rangle \) of the tube in the current state to the tube diameter \( a_0 \) in the reference state, i.e.,
\[
\alpha(F) = \frac{\langle a_n \rangle}{a_0} = \frac{\int |\mathbf{F} \cdot \mathbf{R}|^2 f_0(\mathbf{R}) d^3 \mathbf{R}}{\left( \mathbf{R}_{ee}^2 \right)^{\frac{3}{2}} \frac{|\mathbf{F} \cdot \mathbf{u}_0|}{4\pi} d^2 \mathbf{u}_0}
\] (3.33)

3.3 Constitutive model database

The purpose of establishing the constitutive model database is to select appropriate constitutive models to characterize the viscoelastic response of elastomers by identifying the representative material parameters in such constitutive models. Any variation in the microstructure of elastomers, such as chemical composition, degree of polymerization, extensibility of polymer chains, molecular weight of monomers, cross-linking density, and amount of chain entanglement, may have an essential impact on the macroscopic properties of the material. In order to fulfill the potential applications of these new elastomers, their materials properties should be characterized through fitting appropriate constitutive models to the available experimental data.

In the literature, great efforts have been devoted to developing constitutive models to capture the hyperelastic nature of elastomers. These constitutive models are established either on the basis of continuum mechanics (phenomenological model) or through statistical mechanics treatment [61-63]. For the continuum mechanics treatment, the hyperelastic behavior of the materials are described by means of a strain energy density function involving either strain invariants or principle stretches. The representative models include neo-Hookean model, Mooney-Rivlin model, Yeoh model, Gent model and Ogden model. In general, those models are capable of providing empirical nonlinear stress-strain relationship of the material but lack physical interpretation of the involved physics and chemistry parameters in the constitutive models. While the models developed by statistical mechanics treatment directly link the macroscopic behavior of elastomers to their microstructures represented by the physics and chemistry parameters. Example models include affine network models [25-29, 46, 73], and non-affine network models [30, 82]. Detailed comments on the advantages and limitations of these models can be found from the work of Zhou et al. [42].
To apply the parallel rheological model, both the equilibrium Helmholtz free energy density $W_A \left( F_A \right)$ and the non-equilibrium Helmholtz free energy density $W_{B_{n_e}} \left( F_{B_{n_e}} \right)$ must be specified first. As the equilibrium Helmholtz free energy density is stored in the elastic ground network of the elastomer, the selected strain energy density $W_A \left( F_A \right)$ is used to capture the pure elastic response of the material. Therefore, the material parameters in the strain energy density function $W_A \left( F_A \right)$ can be determined by data fitting to the quasi-static experiments. While the material parameters in the strain energy density function $W_{B_{n_e}} \left( F_{B_{n_e}} \right)$ can be obtained by data fitting to the loading or unloading processes conducted at different loading rates. Since the non-equilibrium Helmholtz free energy density is only related to the elastic deformation of the elastomers, as a common practice in the literature [42, 93], we can assume it as a strain energy density function that can take either the same form or a different form of the strain energy density function of the equilibrium state. In this thesis, six commonly adopted constitutive models, i.e., neo-Hookean model, Mooney-Rivlin model, Yeoh model, Gent model, Ogden model, and non-affine model, are implemented in the database for material model selection and material properties characterization.

Since the experimental stress-strain data are usually obtained from standard uniaxial tests, such as quasi-static tests, cyclic loading-unloading tests and stress relaxation tests, the stress-strain relation according to the six constitutive models mentioned above are derived under the uniaxial loading condition.

3.3.1 Deformation description for elastomers under uniaxial loading

Under uniaxial loading, the elastomer is homogeneously stretched in one direction while the other two directions are free to deform. The stretch ratio in the loading direction is denoted as $\lambda_1 = \lambda, \lambda_{1B_{n_e}}^e = \lambda_n^e, \lambda_{1B_{n_e}}^i = \lambda_n^i$. Elastomers are commonly considered as incompressible, i.e., $\det F_A = \det F_{B_{n_e}} = \det F_{B_{n_e}}^e = \det F_{B_{n_e}}^i = 1$, which gives the stretches in the other two directions as $\lambda_2 = \lambda_3 = \lambda^{-1/2}, \lambda_{n2}^e = \lambda_{n3}^e = \left(\lambda_n^e\right)^{-1/2}$ and $\lambda_{n2}^i = \lambda_{n3}^i = \left(\lambda_n^i\right)^{-1/2}$.
Therefore, the deformation gradient tensor for both the ground network and subnetworks in the parallel rheological model as shown in Figure 3-2 can be expressed as,

\[ F = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-\frac{3}{2}} & 0 \\ 0 & 0 & \lambda^{-\frac{3}{2}} \end{bmatrix}, \quad F^{n}_{B} = \begin{bmatrix} \lambda^{e} & 0 & 0 \\ 0 & (\lambda^{e})^{-\frac{3}{2}} & 0 \\ 0 & 0 & (\lambda^{e})^{-\frac{3}{2}} \end{bmatrix}, \quad F^{n}_{B} = \begin{bmatrix} \lambda^{i} & 0 & 0 \\ 0 & (\lambda^{i})^{-\frac{3}{2}} & 0 \\ 0 & 0 & (\lambda^{i})^{-\frac{3}{2}} \end{bmatrix} \]  

(3.34)

3.3.2 Stress derivation for different constitutive models

The experimental data from the uniaxial tests are often recorded in the form of nominal stress-stretch ratio curves under different loading and unloading conditions. The nominal stress tensor \( \mathbf{N} \) is defined as the transpose of the first Piola-Kirchhoff stress tensor \( \mathbf{P} \), i.e., \( \mathbf{N} = \mathbf{P}^{T} \). Due to the symmetry of deformation gradient tensor under uniaxial loading, the first Piola-Kirchhoff stress is consequently symmetric according to Eq. (3.2), therefore, \( \mathbf{N} = \mathbf{P} \) and thus the nominal stress is still denoted as \( \mathbf{P} \) hereinafter. The nominal stresses along the directions perpendicular to the loading direction are always zero due to the traction free boundary conditions. Therefore, we only need to derive the normal stress along the loading direction according to different constitutive relations.

The modeling framework developed by Zhou et al. [42] is flexible in choosing specific strain energy density function for \( W_{A} \left( \mathbf{F}_{A} \right) \) and \( W_{B_{i}} \left( \mathbf{F}_{B_{i}} \right) \). The strain energy density function is generally expressed in terms of either the invariants of the Cauchy-Green deformation tensor or the principal stretches. The strain energy density function of the six constitutive models in the database is listed in Table 3-1.

<table>
<thead>
<tr>
<th>Constitutive models</th>
<th>Strain energy density function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neo-Hookean Model</td>
<td>( W = C_{1} \left( I_{1} - 3 \right) )</td>
</tr>
</tbody>
</table>
Yeoh Model \[ W = C_{10} (I_1 - 3) + C_{20} (I_1 - 3)^2 + C_{30} (I_1 - 3)^3 \]

Mooney-Rivlin Model \[ W = C_{10} (I_1 - 3) + C_{01} (I_2 - 3) \]

Gent Model \[ W = -\frac{G_{\text{lim}}}{2} \ln \left( \frac{J_{\text{lim}} - I_1 + 3}{J_{\text{lim}}} \right) \]

Nonaffine Model \[ W = \frac{1}{6} G_e \sum_{i=1}^{3} \lambda_i^2 - G_e \lambda_{\text{max}}^2 \ln \left( 3\lambda_{\text{max}}^2 - \sum_{i=1}^{3} \lambda_i^2 \right) + G_e \sum_{i=1}^{3} \left( \lambda_i + \lambda_i^{-1} \right) \]

Ogden Model \[ W = \sum_{k=1}^{K} \frac{\mu_k}{\alpha_k} \left( \lambda_{1_{\alpha_k}}^{\alpha_k} + \lambda_{2_{\alpha_k}}^{\alpha_k} + \lambda_{3_{\alpha_k}}^{\alpha_k} - 3 \right) \]

As shown in this Table, the strain energy density functions of the neo-Hookean model, Yeoh model, Mooney-Rivlin model as well as Gent model are in terms of the three invariants of the right or the left Cauchy-Green deformation tensor \( C = F^T F \) or \( B = F F^T \), i.e.,

\[ I_1 = \text{tr}(C) = \text{tr}(B) \quad (3.35a) \]

\[ I_2 = \frac{1}{2} \left[ \text{tr}(C)^2 - \text{tr}(C^2) \right] = \frac{1}{2} \left[ \text{tr}(B)^2 - \text{tr}(B^2) \right] \quad (3.35b) \]

\[ I_3 = \det(C) = \det(B) \quad (3.35c) \]

Alternatively, these invariants can also be expressed in terms of the principle stretches as,

\[ I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad (3.36a) \]

\[ I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \quad (3.36b) \]

\[ I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2 \quad (3.36c) \]
Particularly, for incompressible materials, $\lambda_1\lambda_2\lambda_3 = 1$ and $I_3 = 1$.

In the following, the specific expressions of the nominal stress $P$ are derived according to different constitutive models for the viscoelastic materials. For simplicity purpose, the elastomers are assumed as isotropic and incompressible, which are under homogeneous deformation.

### 3.3.2.1 neo-Hookean Model

Based on statistical thermodynamics of crosslinked polymer chains, the neo-Hookean model is the simplest model among the commonly used hyperelastic material models. Similar to the generalized Hook’s law, the neo-Hookean model is capable of capturing the nonlinear stress-strain response when the material undergoes large deformation. Typically for strains less than 20%, this model exhibits good capability as the polymer chains in the cross-linked polymers can move relative to each other when subjected to a stress. However, when the polymer chains are stretched to the maximum point that the covalent cross links allow, a remarkable departure of the experimental data from the theoretical results is observed. Due to its simplicity, this neo-Hookean model is still widely used in modeling the hyperelastic behavior of rubber-like materials.

This model was proposed by Rivlin [21], the strain energy density function is expressed in terms of only the first invariant $I_1$ of the right Cauchy-Green deformation tensor for an incompressible elastomer, as

\[
W_A = C_1^{EQ} \left( I_1 - 3 \right)
\]

(3.37a)

\[
W_{B_n} = C_{1n}^{NEQ} \left( I_{1n}^{e} - 3 \right)
\]

(3.37b)

for the equilibrium network $A$ and the nonequilibrium subnetworks $B_n$, respectively. $C_1^{EQ}$ and $C_{1n}^{NEQ}$ are determined in terms of the shear modulus $\mu$ of their corresponding networks, i.e., $C_1^{EQ} = \mu^{EQ} / 2$ and $C_{1n}^{NEQ} = \mu_{n}^{NEQ} / 2$, respectively. $\mu^{EQ}$ and $\mu_{n}^{NEQ}$ are related to the number of polymer chains per unit volume in the corresponding networks $n_A$ and $n_{B_n}$, as
\( \mu_{\alpha}^{EQ} = n_{\alpha} k_B T \) and \( \mu_{b_{\alpha}}^{NEQ} = n_{b_{\alpha}} k_B T \) with \( k_B \) being the Boltzmann’s constant and \( T \) being the absolute temperature.

According to Eqs. (3.12) and (3.16), the equilibrium and non-equilibrium nominal stresses (first Piola-Kirchhoff stresses) along the loading direction are determined for incompressible materials, as,

\[
\left( P_{\alpha}^{EQ}\right)_{nH} = 2C_{1}^{EQ} \left( \lambda - \lambda^{-2} \right) \tag{3.38a}
\]

\[
\left( P_{b_{\alpha}}^{NEQ}\right)_{nH} = 2C_{1n}^{NEQ} \left[ \lambda \left( \lambda^{-1}_n \right)^{-1} - \lambda^{-2}_n \left( \lambda^{-1}_n \right)^{-2} \right] \tag{3.38b}
\]

For any given stretch ratio \( \lambda \) which can be measured under different loading rates in the uniaxial tests, the inelastic stretch ratio \( \lambda^{-1}_n \) of each individual subnetwork \( B_n \) must fulfill the evolution law of thermodynamics in Eq. (3.21), i.e.,

\[
d \frac{\lambda^{-1}_n}{dt} = \frac{2\alpha F}{3\eta_{n0}} C_{1n}^{NEQ} \left[ \lambda^{-2}_n \left( \lambda^{-1}_n \right)^{-2} \right] \tag{3.39}
\]

### 3.3.2.2 Mooney-Rivlin Model

Postulated by Mooney [44] and further developed by Rivlin [21] and Rivlin and Saunders [47], the Mooney-Rivlin model, as a special case of the generalized Rivlin model and an extension of the neo-Hookean model, is usually adopted to describe the hyperelastic behavior of rubber-like materials particularly under large deformation up to 100\%. In this Mooney-Rivlin model, the two-parameter strain energy density function is expressed in terms of the first and second invariants \( I_1 \) and \( I_2 \), as,

\[
W_{\alpha}^{EQ} = C_{10}^{EQ} (I_1 - 3) + C_{01}^{EQ} (I_2 - 3) \tag{3.40a}
\]

\[
W_{b_{\alpha}}^{NEQ} = C_{10n}^{NEQ} (I_{1n}^r - 3) + C_{01n}^{NEQ} (I_{2n}^r - 3) \tag{3.40b}
\]
for both the equilibrium and non-equilibrium states. The two parameters $C_{10}$ and $C_{01}$ are related to the shear modulus $\mu$, i.e., $\mu = C_{10} + C_{01}$, with the superscript ‘EQ’ and ‘NEQ’ representing the quantity for the equilibrium network A and the non-equilibrium subnetworks Bn, respectively. To produce real material response, the values of $C_{10}$ and $C_{01}$ should obey $C_{10} + C_{01} \geq 0$ and $C_{01} > 0$ [98] in accordance with the stability criterion [99]. When $C_{01} = 0$, the Mooney-Rivlin model reduces to the neo-Hookean model.

With the adoption of multiplicative decomposition, the elastic and inelastic first Piola-Kirchhoff stresses along the loading direction are formulated as,

\[
\left( P_{EQ}^{MR} \right) = 2C_{10}^{EQ} \left( \lambda - \lambda^{-2} \right) + 2C_{01}^{EQ} \left( 1 - \lambda^{-3} \right) \tag{3.41a}
\]

\[
\left( P_{Bn}^{NEQ} \right) = 2C_{10n}^{NEQ} \lambda \left( \lambda_n^i \right)^{-1} - \lambda^{-2} \left( \lambda_n^i \right)^2 + 2C_{01n}^{NEQ} \left[ 1 - \lambda^{-3} \left( \lambda_n^i \right)^3 \right] \tag{3.41b}
\]

in which the inelastic stretch ratio $\lambda_n^i$ is determined from the evolution law of thermodynamics in Eq. (3.21) as,

\[
\frac{d\lambda_n^i}{dt} = 2\alpha \left( \frac{F}{3} \right)^2 \frac{\lambda_n^i}{\eta_{n0}} \left\{ C_{10n}^{NEQ} + C_{01n}^{NEQ} \left[ \frac{\lambda_n}{\lambda_n^i} \right]^2 + 2 \frac{\lambda_n}{\lambda_n^i} \right\} \left[ \frac{\lambda}{\lambda_n^i} \right]^2 - C_{01n}^{NEQ} \left[ \frac{\lambda}{\lambda_n^i} \right]^4 \right\} \tag{3.42}
\]

\[
\frac{d\lambda_n^i}{dt} = 2\alpha \left( \frac{F}{3} \right)^2 \frac{\lambda_n^i}{\eta_{n0}} \left\{ C_{10n}^{NEQ} + C_{01n}^{NEQ} \left[ \frac{\lambda}{\lambda_n^i} \right]^2 + 2 \frac{\lambda_n}{\lambda_n^i} \right\} \left[ \frac{\lambda}{\lambda_n^i} \right]^2 - C_{01n}^{NEQ} \left[ \frac{\lambda}{\lambda_n^i} \right]^4 \right\} \tag{3.42}
\]

### 3.3.2.3 Yeoh Model

In addition to the neo-Hookean and the Mooney-Rivlin models, researchers have also attempted to develop models to capture the hyperelastic behavior of elastomeric materials by using strain energy functions which involve some higher order terms of the strain invariants. The Yeoh model [23] is one of these phenomenological models for describing the deformation of nearly incompressible and nonlinear elastic materials. It is found that the Yeoh model works better in capturing moderate to large deformation of rubbers and is
capable of capturing the variation of shear modulus during the deformation of vulcanized carbon black-filled rubbers [23]. For this model, the strain energy density function is formulated as a cubic polynomial of the first invariant of the Cauchy-Green deformation tensor for incompressible rubbers, as

\[ W_A^{EQ} = C_{10}^{EQ} (I_1 - 3) + C_{20}^{EQ} (I_1 - 3)^2 + C_{30}^{EQ} (I_1 - 3)^3 \]  

(3.43a)

\[ W_B_{n}^{NEQ} = C_{10n}^{NEQ} (I_{1n}^e - 3) + C_{20n}^{NEQ} (I_{1n}^e - 3)^2 + C_{30n}^{NEQ} (I_{1n}^e - 3)^3 \]  

(3.43b)

for both the equilibrium and non-equilibrium states. The coefficients \( C_{10}, C_{20}, C_{30} \) with superscript “EQ” and “NEQ” are relevant to the variable shear modulus \( \mu \) of the ground network and the individual subnetwork. To satisfy the variation of the shear modulus, the constraints that \( C_{20} < 0 \) while \( C_{10} \) and \( C_{30} > 0 \) should be added in the parameter identification process.

Then the equilibrium and the non-equilibrium first Piola-Kirchhoff stresses along the loading direction are derived from these strain energy density functions as,

\[ (P_{A}^{EQ})_Y = 2(\lambda - \lambda^{-2})\left[ C_{10}^{EQ} + 2C_{20}^{EQ} (\lambda^2 + 2\lambda^{-1} - 3) + 3C_{30}^{EQ} (\lambda^2 + 2\lambda^{-1} - 3)^2 \right] \]  

(3.44a)

\[ (P_{B,n}^{NEQ})_Y = 2\left[ \lambda^2 (\lambda_n^e)^{-1} - \lambda^{-2} (\lambda_n^e)^2 \right]\left[ C_{10n}^{NEQ} + 2C_{20n}^{NEQ} \left[ \lambda^2 (\lambda_n^e)^{-1} - 2\lambda^{-1} (\lambda_n^e)^{-3} \right] \right] \]  

(3.44b)

\[ + 3C_{30n}^{NEQ} \left[ \lambda^2 (\lambda_n^e)^{-1} - 2\lambda^{-1} (\lambda_n^e)^{-3} \right]^2 \}

Again, the time-dependent inelastic stretch ratio for each subnetwork in the nominal stress expression is determined from the thermodynamics evolution law Eq. (3.21), i.e.,

\[ \frac{d \lambda_n^{i}}{dt} = \frac{2\alpha (\mathbf{F})^2}{3\eta_0} \left[ \lambda^2 (\lambda_n^{i})^{-1} - \lambda^{-2} (\lambda_n^{i})^2 \right]\left[ C_{10n}^{NEQ} + 2C_{20n}^{NEQ} \left[ \lambda^2 (\lambda_n^{i})^{-1} - 2\lambda^{-1} (\lambda_n^{i})^{-3} \right] \right] \]  

(3.45)
3.3.2.4 Gent Model

It should be noted that the constitutive models mentioned above do not take the material extensibility (the limit of the stretch) into account. However, in a real polymer network, there is a limit of the extension of the polymer chains. To account for such material extensibility, Gent [24] proposed a phenomenological model for rubber elasticity. In this model, the strain energy density function is designed to possess a singularity when the first invariant $I_1$ reaches a limiting value $I_m$, i.e., $I_m=J_{lim}+3$. When $I_m \to \infty$, the Gent model reduces to the neo-Hookean model. The corresponding strain energy density functions for the equilibrium and the non-equilibrium states are given as,

$$W_{A_{EQ}} = -\frac{G_{EQ}}{2} J_{lim} \ln \left(1 - \frac{I_1 - 3}{J_{lim}}\right)$$  \hspace{1cm} (3.46a)  

$$W_{B_{NEQ}} = -\frac{G_{n_{NEQ}}}{2} J_{lim} \ln \left(1 - \frac{I_m - 3}{J_{lim}}\right)$$  \hspace{1cm} (3.46b)

where $J_{lim}$ represents the extensibility of the elastomer, which is related to the degree of polymerization $N$, i.e., $J_{lim} = 3(N-1)$ [71]. $G_{EQ}$ and $G_{n_{NEQ}}$ are the macroscale shear modulus of the ground network and the subnetworks, respectively. Both of them are related to the number of polymer chains per unit volume in the corresponding network, i.e., $G_{EQ} = n_A k_B T$ and $G_{n_{NEQ}} = n_{B_n} k_B T$ with $n_A$ and $n_{B_n}$ being the number of polymer chains per unit volume in the ground network $A$ and the subnetwork $B_n$, respectively. Due to the logarithm expression of the strain energy density function, the stretch ratios need to satisfy $\left[1-(I_1 - 3)/J_{lim}\right] > 0$, while the maximum stretch ratio is limited by the extensibility value.

From these strain energy density functions, the first Piola-Kirchhoff stress along the loading direction in both the equilibrium and non-equilibrium states are expressed as,

$$\left(P_{EQ}^E\right) = \frac{G_{EQ}}{J_{lim} - \lambda^2 - 2\lambda^{-1} + 3} \left(\lambda - \lambda^{-2}\right)$$  \hspace{1cm} (3.47a)
\[
\left( p^{\text{NEQ}}_n \right)_G = \frac{G^{\text{NEQ}}_n J_{\text{lim}}}{J_{\lim} - \frac{1}{\lambda} \left( \frac{\lambda}{\lambda_n^i} \right)^2 - 2 \frac{1}{\lambda} \left( \frac{\lambda}{\lambda_n^i} \right)^3 + 3} \left[ \frac{\lambda}{\lambda_n^i} - \frac{1}{\lambda} \left( \frac{\lambda}{\lambda_n^i} \right)^2 \right]
\] (3.47b)

According to the thermodynamics evolution law Eq. (3.21), the time-dependent inelastic stretch rate is determined as,

\[
\frac{d \lambda_n^i}{dt} = \frac{G^{\text{NEQ}}_n J_{\text{lim}} \alpha(F)^2}{3 \eta_0 J_{\lim} - \frac{1}{\lambda^2} \left( \frac{\lambda}{\lambda_n^i} \right)^2 - 2 \frac{1}{\lambda^2} \left( \frac{\lambda}{\lambda_n^i} \right)^3 + 3} \left[ \frac{\lambda^2}{\lambda_n} - \frac{1}{\lambda} \left( \frac{\lambda}{\lambda_n^i} \right)^2 \right]
\] (3.48)

### 3.3.2.5 Nonaffine Model

The nonaffine model [30] was developed to capture the effects of both the cross-linking density and the entanglement of polymer chains on the macroscopic behavior of elastomers under finite deformation. As the entanglement network is analyzed through a tube model, the strain energy density function is a combination from both the crosslinked network and tube component, which is expressed in terms of the first invariant \( I_1 \) and the three principal stretches, as

\[
W = \frac{1}{6} G_e I_1 - G_e \lambda_{\text{max}}^2 \ln \left( 3 \lambda_{\text{max}}^2 - I_1 \right) + G_e \left( \frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3} \right) + G_e \left( \frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3} \right)
\] (3.49)

where \( G_e \) is the modulus of the crosslinked network, defined as \( G_e = k_b T \rho_m g^2 (1 - 2\phi) / N \), while \( G_e \) is the entanglement modulus, defined as \( G_e = k_b T \rho_m / (2N_e) \)[30]. \( \rho_m \) is the mass density of monomer, \( N \) is the number of chains connected at a crosslink, \( \phi \) is the functionality of cross-linkers, \( g \) is the affinity function of polymer chain length under deformation, and \( N_e \) represents the number of monomers between two entanglements [30]. \( \lambda_{\text{max}} \) is the maximum stretch of the primitive chain in the affine tube, determined as \( \lambda_{\text{max}} = \sqrt{N/(1 - 2/\phi)} / g \) [30].
The strain energy density function in the equilibrium and the non-equilibrium states are given as,

\[
W_{\text{EQ}}^A = \frac{1}{6} G_{\text{c}}^{\text{EQ}} I_1 - G_{\text{c}}^{\text{EQ}} \lambda_{\text{max}}^2 \ln \left(3 \lambda_{\text{max}}^2 - I_1 \right) + G_{\text{c}}^{\text{EQ}} \left( \lambda_1 + \frac{1}{\lambda_1} + \lambda_2 + \frac{1}{\lambda_2} + \lambda_3 + \frac{1}{\lambda_3} \right)
\]  

(3.50a)

\[
W_{\text{NEQ}}^{B_A} = \frac{1}{6} G_{\text{cn}}^{\text{NEQ}} I_1^e - G_{\text{cn}}^{\text{NEQ}} \lambda_{\text{max}}^e \ln \left(3 \lambda_{\text{max}}^e - I_1^e \right) + G_{\text{cn}}^{\text{NEQ}} \left( \lambda_{1n}^e + \frac{1}{\lambda_{1n}^e} + \lambda_{2n}^e + \frac{1}{\lambda_{2n}^e} + \lambda_{3n}^e + \frac{1}{\lambda_{3n}^e} \right)
\]  

(3.50b)

Correspondingly, the first Piola-Kirchhoff stress along the loading direction in the equilibrium and non-equilibrium states takes the following forms,

\[
\left( P_{\text{EQ}}^{B_A} \right)_{\text{NA}} = \frac{1}{3} G_{\text{c}}^{\text{EQ}} \left( \lambda - \lambda^{-2} \right) + \frac{G_{\text{c}}^{\text{EQ}} \lambda_{\text{max}}^2 \left(2 \lambda - 2 \lambda^{-2} \right)}{3 \lambda_{\text{max}}^2 - \lambda^2 - 2 \lambda^{-1}} + G_{\text{c}}^{\text{EQ}} \left(1 - \lambda^{-2} + \lambda^{-1} \lambda^2 - \lambda^{-2} \right)
\]  

(3.51a)

\[
\left( P_{\text{NEQ}}^{B_A} \right)_{\text{NA}} = \frac{1}{3} G_{\text{cn}}^{\text{NEQ}} \left[ \lambda \left( \lambda_n^i \right)^{-1} - \lambda^{-2} \left( \lambda_n^i \right)^2 \right] + G_{\text{cn}}^{\text{NEQ}} \lambda_{\text{max}}^2 \left[ \frac{2 \lambda \left( \lambda_n^i \right)^{-1} - 2 \lambda^{-3} \left( \lambda_n^i \right)^2}{3 \lambda_{\text{max}}^2 - \lambda^2 \left( \lambda_n^i \right)^2 - 2 \lambda^{-1} \lambda_n^i} \right]
\]  

\[
+ G_{\text{cn}}^{\text{NEQ}} \left[ 1 - \lambda^{-2} \left( \lambda_n^i \right)^2 - \lambda^{-2} \left( \lambda_n^i \right)^3 + \lambda^{-2} \left( \lambda_n^i \right)^3 \right]
\]  

(3.51b)

The time-dependent inelastic stretch ratio is determined by employing the thermodynamics evolution law of Eq. (3.21), as

\[
\frac{d \lambda_n^i}{dt} = \frac{\lambda_n^i \alpha (F)^2}{3 \eta_0} \left[ \frac{1}{3} G_{\text{cn}}^{\text{NEQ}} \left( \lambda_n^2 \left( \lambda_n^i \right)^{-2} - \lambda_n^{-1} \lambda_n^i \right) + \frac{2 G_{\text{cn}}^{\text{NEQ}} \lambda_{\text{max}}^2 \left[ \lambda_n^2 \left( \lambda_n^i \right)^{-2} - \lambda_n^{-1} \lambda_n^i \right]}{3 \lambda_{\text{max}}^2 - \lambda^2 \left( \lambda_n^i \right)^2 - 2 \lambda^{-1} \lambda_n^i} \right]
\]  

\[
+ \frac{\lambda_n^i \alpha (F)^2 G_{\text{cn}}^{\text{NEQ}}}{3 \eta_0} \left[ \lambda_n \left( \lambda_n^i \right)^{-1} + \lambda_n^2 \left( \lambda_n^i \right)^{-1} \right]
\]  

(3.52)
3.3.2.6 Ogden Model

For the continuum mechanics treatment, the strain energy density function can be either invariant-based or stretch-based. The Ogden model [22] is one of the stretch-based phenomenological models used to describe the nonlinear stress-strain behavior of soft materials, with the strain energy density function proposed as,

$$ W = \sum_{k=1}^{K} \frac{\mu_k}{\alpha_k} \left( \lambda_1^{\alpha_k} + \lambda_2^{\alpha_k} + \lambda_3^{\alpha_k} - 3 \right) $$

where $\mu_k$ and $\alpha_k$ are material constants that fulfill the constraint $\mu_k \alpha_k > 0$ in accordance with the Hill stability criterion [68]. The shear modulus is determined from the statement $2\mu = \sum_{k=1}^{K} \mu_k \alpha_k$ and $K$ is usually taken as 3 to accurately describe the nonlinear response of rubber-like materials. For the particular values of $K$ and $\alpha_k$, the Ogden model will reduce to either the neo-Hookean model or the Mooney-Rivlin model.

Taking $K=3$, the strain energy density function in the equilibrium and the non-equilibrium states are expressed as,

$$ W_A^{EQ} = \sum_{k=1}^{3} \frac{\mu_k}{\alpha_k} \left[ \lambda_1^{\alpha_k} + \lambda_2^{\alpha_k} + \lambda_3^{\alpha_k} - 3 \right] $$

$$ W_{B_n}^{NEQ} = \sum_{n=1}^{N} \sum_{k=1}^{3} \frac{\mu_{k_n}}{\alpha_{k_n}} \left[ \left( \lambda_1^{\alpha_{k_n}} \right)^{\alpha_{k_n}} + \left( \lambda_2^{\alpha_{k_n}} \right)^{\alpha_{k_n}} + \left( \lambda_3^{\alpha_{k_n}} \right)^{\alpha_{k_n}} - 3 \right] $$

Correspondingly, the first Piola-Kirchhoff stress along the loading direction in the equilibrium and the non-equilibrium states takes the form of,

$$ \left( P^{EQ} \right)_O = \sum_{k=1}^{3} \mu_k^{EQ} \left( \lambda^{\alpha_k^{EQ} - 1} - \frac{\alpha_k^{EQ} - 1}{2} \right) $$
\[
(P^{NEQ}_{B_e})_O = \sum_{n=1}^{N} \sum_{k=1}^{3} \mu^{NEQ}_{kn} \lambda^\alpha_{kn}^{\alpha_{NEQ}-1} \left( \lambda^i_n \right)^{\alpha_{NEQ}^{\alpha_{NEQ}-1} + 1} - \lambda \left( \lambda^i_n \right)^{\frac{1}{2} \alpha_{kn}^{\alpha_{NEQ}-1} + 1}
\]

(3.55b)

The time-dependent inelastic stretch ratio is determined by adopting the thermodynamics evolution law Eq. (3.21),

\[
\frac{d \lambda^i_n}{dt} = \frac{\lambda^i_n \alpha (F)^2}{3 \eta_{n0}} \sum_{n=1}^{N} \sum_{k=1}^{3} \mu^{NEQ}_{kn} \left[ \lambda^\alpha_{kn}^{\alpha_{NEQ}-1} \left( \lambda^i_n \right)^{-\alpha_{NEQ}^{\alpha_{NEQ}-1}} - \lambda \left( \lambda^i_n \right)^{-\frac{1}{2} \alpha_{kn}^{\alpha_{NEQ}-1}} \right]
\]

(3.56)

The derived nominal stresses from these hyperelastic models are stored in the constitutive model database, which is designed to consist of two sections. The equilibrium nominal stress \( P^{EQ} \) derived from different constitutive relations are put in the equilibrium section, while the non-equilibrium nominal stress \( P^{NEQ} \) and the inelastic stretch ratio \( \lambda^i_n \) fulfilling the thermodynamics evolution law are stored in the non-equilibrium section. In each section, the material parameters need to be determined through data fitting with experimental data are listed in Table 3-2.

<table>
<thead>
<tr>
<th>Constitutive models</th>
<th>Equilibrium parameters</th>
<th>Nonequilibrium parameters of each subnetwork (n=1, 2, … N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neo-Hookean Model</td>
<td>( C_1^{EQ} )</td>
<td>( C_{1n}^{NEQ}, \eta_{n0} )</td>
</tr>
<tr>
<td>Yeoh Model</td>
<td>( C_{10}^{EQ}, C_{20}^{EQ}, C_{30}^{EQ} )</td>
<td>( C_{10n}^{NEQ}, C_{20n}^{NEQ}, C_{30n}^{NEQ}, \eta_{n0} )</td>
</tr>
<tr>
<td>Mooney-Rivlin Model</td>
<td>( C_1^{EQ}, C_0^{EQ} )</td>
<td>( C_{10n}^{NEQ}, C_{01n}^{NEQ}, \eta_{n0} )</td>
</tr>
<tr>
<td>Gent Model</td>
<td>( G^{EQ}, J_{lim} )</td>
<td>( G_{n}^{NEQ}, J_{lim}, \eta_{n0} )</td>
</tr>
<tr>
<td>Nonaffine Model</td>
<td>( G_e^{EQ}, A_{max} )</td>
<td>( G_{e0}^{NEQ}, G_{e0}^{NEQ}, \eta_{n0}, \lambda_{max} )</td>
</tr>
</tbody>
</table>
In order to characterize the material properties, the constitutive model selection and the material parameters identification will be performed simultaneously in the process. This constitutive model database exhibits great flexibility and diversity in selecting appropriate material models and characterizing material properties. As a common practice in the literature [38, 42, 48, 91, 93], the non-equilibrium strain energy density function can be flexibly selected either the same format or the different format as the equilibrium strain energy density function depending on the macroscopic performance of the material. In the current database, there are six choices available for both the equilibrium and the non-equilibrium strain energy density function, which will give 36 model configurations in total for material model selection. With the development of new constitutive models, these new models can certainly be added to the current framework, leading to more options for material model selection. Moreover, it is flexible to choose the total number \( N \) of different types of viscous subnetworks. It should also be mentioned that the equilibrium and the non-equilibrium material parameter identification processes are conducted separately with the consideration of computational cost if possible.

### 3.4 Selection procedure in parameter identification process

After establishing the constitutive model database, in this section, a fitting and selecting process is introduced to identify the most suitable constitutive models and the corresponding material property parameters for describing the viscoelastic response of elastomers.

#### 3.4.1 Genetic algorithm

Genetic algorithm (GA), introduced by John Holland [100], was developed based on the natural selection process [101] that imitates biological evolution to choose the fittest individuals from a population, which has been widely utilized for data fitting and optimization problems. The operation process of genetic algorithm is shown in Figure 3-8.
The process begins with a set of candidates as the initial population. Each candidate is characterized by a set of properties known as genes. In order to evaluate how fit a candidate is, the fitness value of each candidate is calculated according to the fitness function, which is associated with the given problem. Then, the fittest candidates are selected, and their properties are allowed to pass to the next generation by crossover and mutation. Fitter candidates keep evolved in the iterative process till stopping criterion is satisfied. Generally, the genetic algorithm terminates when there is no significant difference of the evolved candidates from the previous generation to the current generation.

![Operation flow chart of Genetic Algorithm](image)

*Figure 3-8 The operation flow chart of Genetic Algorithm*

In MATLAB, a toolbox is available for the optimization using GA, with the command expression as,

\[
[v, fval] = ga(func, nvars, lb, ub)
\]  

(3.57)

where \(v\) and \(fval\) are the output of the ‘ga’ function, while \(func, nvars, lb\) and \(ub\) are the inputs of the ‘ga’ function. \(v\) is the fitting parameter vector, \(fval\) is related to the fitness
function, \( nvars \) is the total number of the to-be-determined variables, \( lb \) and \( ub \) are the lower bound and upper bound of the to-be-determined variables. For data fitting, the fitness function \( \text{func} \) is the discrepancy between the theoretical value and the experimental data, i.e.,

\[
\text{func} = P_{\text{theoretical}} - P_{\text{experimental}}
\]  

(3.58)

In this case, \( P_{\text{experimental}} \) is defined as a stress vector to store the measured nominal stress data from the uniaxial tension tests, while \( P_{\text{theoretical}} \) is the stress vector to store the theoretical nominal stress along the loading direction calculated according to different constitutive models. The Root-mean-square error (\( \text{RMSE} \)) between the data from the experiment and the theoretical simulation is defined as \( fval \) to assess the quality of data fitting on the global scale, which is defined as [102],

\[
fval = \text{RMSE} = \sqrt{\frac{\sum_{m=1}^{M} \left( P_{\text{theoretical}}(m) - P_{\text{experimental}}(m) \right)^2}{M}}
\]  

(3.59)

where \( M \) is the number of experimental data points. According to Eq. (3.59), the value of the \( \text{RMSE} \) is a non-negative number, i.e., \( \text{RMSE} \geq 0 \). A lower \( \text{RMSE} \) means a better data fitting between the theoretical simulations and the experimental data, with a value of zero (impossible to achieve in practice) representing a perfect data fitting. Therefore, the optimization of those to-be-determined parameters inside the ‘ga’ function is conducted by minimizing the value of \( fval \).

To calculate \( P_{\text{theoretical}} \) in the fitness function \( \text{func} \) for the six constitutive models in the database, the output parameter vector \( \mathbf{v} \) for the equilibrium and the non-equilibrium states is prescribed as,

\[
\mathbf{v}^{\text{EQ}} = \left[ C_{1}^{\text{EQ}}, C_{10}^{\text{EQ}}, C_{2}^{\text{EQ}}, C_{20}^{\text{EQ}}, C_{3}^{\text{EQ}}, C_{30}^{\text{EQ}}, G_{\text{lim}}^{\text{EQ}}, J_{\text{lim}}^{\text{EQ}}, G_{r}^{\text{EQ}}, G_{s}^{\text{EQ}}, \mu_{\max}^{\text{EQ}}, \mu_{1}^{\text{EQ}}, \mu_{2}^{\text{EQ}}, \mu_{3}^{\text{EQ}}, a_{1}^{\text{EQ}}, a_{2}^{\text{EQ}}, a_{3}^{\text{EQ}}, x, y, z, a, b \right]
\]  

(3.60a)
\[ \mathbf{v}^{\text{NEQ}} = [C_{1n}^{\text{NEQ}}, \eta_n^{\text{NEQ}}, C_{10n}^{\text{NEQ}}, C_{20n}^{\text{NEQ}}, C_{30n}^{\text{NEQ}}, \eta_n^{0}, C_{10n}^{\text{NEQ}}, C_{01n}^{\text{NEQ}}, \eta_n^{0}, G_{B_n}^{\text{NEQ}}, \eta_n^{0}, \eta_n^{0}, \eta_n^{0}] \]

The lower and upper bounds of the equilibrium parameter vector \( \mathbf{v}^{EQ} \) and the nonequilibrium parameter vector \( \mathbf{v}^{NEQ} \) are assigned as inputs \( \mathbf{lb} \) and \( \mathbf{ub} \), respectively. The initial guesses of these two vectors are randomly generated by ‘ga’ function and are used to calculate the corresponding theoretical nominal stress \( P_{\text{theoretical}} \) according to the six constitutive models. The parameter set \([x, y, z, a, b]\) located in the latter part of the parameter vector implements the selection procedure which will be explained in the following section. Similarly, the initial guess of \([x, y, z, a, b]\) is also a random parameter set generated by the ‘ga’ function within the range of [0,1] for each element. The optimization of these parameters inside the ‘ga’ function is accomplished by minimizing the value of \( fval \), namely the RMSE, between the data from experiments and theoretical simulations that are calculated in accordance with the internal-fitted parameters. ‘ga’ function uses four stopping criteria to determine when to terminate the solver. ‘ga’ function stops when it reaches the maximum time limit or the maximum number of generations which is 100 times the number of the to-be-determined variables \( nvars \) by default. ‘ga’ function also terminates when the population satisfies the convergence criteria, in other words, the value of \( fval \) does not change over the stall time or the stall generations set by default. It is judged by the average variation of the value of \( fval \) over the stall time or the stall generations, which is smaller than the default tolerance \( 10^{-6} \). Stall time (or generations) is to ensure a minimum number of generations are computed. This process will terminate and output the determined parameter vector \( \mathbf{v} \) when the any of the stopping criteria is satisfied.

In order to eliminate the effect of uncertainty which attributes to the crossover and mutation processes of the ‘ga’ function, the above-mentioned optimization process is repeated for several times with the narrower range of \( \mathbf{lb} \) and \( \mathbf{ub} \) which is adjusted according to the output.
material parameter vector in the previous step. Until a small and acceptable value of \( f_{\text{val}} \) is observed among these optimization processes, the constitutive model is identified, and corresponding material parameters are determined from the output parameter vector.

### 3.4.2 Selection procedure

The material parameters for the equilibrium network are independent of the stretch rate and the viscosity, so that they can be fitted first from the quasi-static loading condition. When the loading rate is very low which can be considered as a quasi-static loading condition, the elastomer is assumed as in an equilibrium state at every instant with \( \lambda_{\text{in}} = \lambda \). In this case, only the first term in Eq. (3.15) for the first Piola-Kirchhoff stress remains when calculating the theoretical nominal stress. Therefore, the theoretical nominal stress in the fitness function is given by the weighted summation [103-104] of the equilibrium nominal stresses of different constitutive models, i.e.,

\[
P_{\text{theoretical}} = P_{\text{EQ}} = p \times (P_{\text{EQ}})_n + q \times (P_{\text{EQ}})_y + r \times (P_{\text{EQ}})_y + s \times (P_{\text{EQ}})_y + t \times (P_{\text{EQ}})_y + u \times (P_{\text{EQ}})_y \quad (3.61)
\]

The weighting coefficients \([p, q, r, s, t, u]\) must meet the condition that only one of them equals to one while the rest are zero so that only one constitutive model is fitted to the experimental data for the purpose of optimization. In this case, the values of the weighting coefficients \([p, q, r, s, t, u]\) are controlled by the parameter set \([x, y, z, a, b]\) through the MATLAB ‘round’ function, which is expressed as,

\[
p = \text{round}(x) \quad (3.62)
\]

\[
q = (1 - p) \times \text{round}(y)
\]

\[
r = (1 - p) \times (1 - q) \times \text{round}(z)
\]

\[
s = (1 - p) \times (1 - q) \times (1 - r) \times \text{round}(a)
\]

\[
t = (1 - p) \times (1 - q) \times (1 - r) \times (1 - s) \times \text{round}(b)
\]

\[
u = (1 - p) \times (1 - q) \times (1 - r) \times (1 - s) \times (1 - t)
\]

For example, if the determined value of \( x \) is 0.8 which is larger than 0.5, then \( p \) is set to equal to one while the other weighting coefficients are zero regardless of the values of \([y, z, a, b]\). Therefore, once the values of set \([x, y, z, a, b]\) are fitted, the values of the weighting
coefficients \([p, q, r, s, t, u]\) are determined. It should be noted that the material model selection and material property parameters identification are performed simultaneously until a small and acceptable value of \(f_{\text{val}}\) is obtained, and one of the weighting coefficients equals 1. Then the constitutive model with the weighting coefficient equal to one is selected, and the material property parameters are identified simultaneously, which are read from the output parameter vector \(v^{\text{EQ}}\) of the “ga” function.

After obtaining the material parameters for the strain energy density function in the equilibrium state, the proper non-equilibrium constitutive model will be selected from the constitutive model database and hence the non-equilibrium material parameters will be identified simultaneously through the data fitting with the measured nominal stress in the experiments under different loading rates. With the consideration of the material viscosity, the theoretical nominal stress is calculated by Eq. (3.15). The determined material parameters in the equilibrium strain energy density function will be used to calculate the corresponding equilibrium nominal stress. Then the theoretical nominal stress in the fitness function is given by the weighted summation of the non-equilibrium nominal stresses of different constitutive models, i.e.,

\[
P_{\text{theoretical}} = P_{\text{EQ}}^{\text{selected}} + p' \sum_{n=1}^{N} \left( P_{\text{NEQ}}^{\text{selected}} \right)_{nG} \left( F_{B_n}^{i} \right)^{-1} + q' \sum_{n=1}^{N} \left( P_{\text{NEQ}}^{\text{selected}} \right)_{nF} \left( F_{B_n}^{i} \right)^{-1} + r' \sum_{n=1}^{N} \left( P_{\text{NEQ}}^{\text{selected}} \right)_{nMR} \left( F_{B_n}^{i} \right)^{-1} (3.63)
\]

where \(P_{\text{EQ}}^{\text{selected}}\) is the equilibrium nominal stress calculated by using the selected equilibrium constitutive model. It should also be mentioned that it is flexible to choose the number of different types of diffusive polymer chains for different constitutive relations, i.e., \(N\) could be selected as different numbers for different models. The weighting coefficients \([p', q', r', s', t', u']\) and the non-equilibrium material parameters for the selected constitutive model will be determined simultaneously from the data fitting with the experimental data following the same way when selecting the equilibrium constitutive model. Finally, a combination of equilibrium and non-equilibrium constitutive models is determined from the database with 36 possible configurations. The material characterization package is thus
developed, consisting of the constitutive model database and the procedures for model selection and material property identification.
Chapter 4

4 Material Property Characterization Results and Discussions

The previous Chapter focuses on elaborating the development of the material characterization package, including the fundamental framework, the constitutive model database and the corresponding procedures for material model selection and material parameter identification. In this Chapter, the capacity and the feasibility of developed material characterization package will be assessed. As there are limited experimental data in the literature, the assessment is only performed on three commonly used elastomeric materials with available data under uniaxial tests, including VHB 4910, HNBR 50 and carbon black (CB) filled elastomers.

4.1 Material property characterization for VHB 4910

The unfilled elastomer VHB 4910 is first selected to assess the developed material characterization package in the current work. As mentioned in the last Chapter, when the material is under a quasi-static loading condition, the material can be considered as in an equilibrium state, i.e., a relaxed condition with \( \lambda_i^\varepsilon = \lambda \) at every moment. Under this loading condition, the nominal stress equals to the equilibrium nominal stress. Therefore, the equilibrium constitutive model and the equilibrium material parameters in accordance with this constitutive model can be determined by fitting the theoretical nominal stress to the experimental data. The experimental data of VHB 4910 under a uniaxial tensile test with low stretching rate (\( \dot{\lambda} = 0.9 \times 10^{-4} / s \)) [49] is plotted in Figure 4-1, which can be considered as a quasi-static loading condition. Here we will use this set of data to select the equilibrium constitutive model and identify the corresponding material parameters. For the equilibrium material parameter selecting, the number of the to-be-determined parameters, i.e., \( nvars \) in the “ga” function of Eq. (3.57), is set as the total number of the equilibrium material parameters of the six constitutive models as listed in Table 3-2 in the last Chapter plus 5, i.e., \( nvars = 22 \). As the first step, the lower bound \( lb \) and the upper bound \( ub \) of the
equilibrium parameter vector \( v^{EQ} \), i.e., the input of the “ga” function, are manually set with a relative wider range. Then the initial values of equilibrium parameter vector \( v^{EQ} \) can thus be randomly generated by the “ga” function, which will be used to calculate the theoretical nominal stresses according to different stretch ratios. These calculated stresses, along with the experimental nominal stress, will be used to define the fitness function \( func \), which is another input for the “ga” function. After all the inputs of the “ga” function are assigned, the “ga” function is run for iterative optimization to return the output, i.e., the parameter vector \( v \), which gives the selected constitutive model and the corresponding material parameters for the equilibrium state. The calculation of the ‘ga’ function will be repeated for the optimization purpose by manually adjusting the lower bound and the upper bound of the equilibrium parameter vector \( v^{EQ} \) within a narrower range until a small and acceptable value of \( fval \) is obtained. In this case, the Gent model is selected as the equilibrium constitutive model and the corresponding material parameters \( G^{EQ} \) and \( J_{\text{lim}} \) are obtained as listed in Table 4-1. The Gent model with the determined values of \( G^{EQ} \) and \( J_{\text{lim}} \) are validated by the excellent agreement between the theoretical nominal stress-stretch curve and the experimental data under quasi-static load as shown in Figure 4-1(a). Following the work of Zhou et al. [42], a model configuration is also conducted by manually selecting the Gent model as the equilibrium constitutive model. The material parameters are identified by data fitting of the theoretical nominal stress-stretch relation to the experimental data as shown in Figure 4-1(b), which are listed in Table 4-2.

Table 4-1 Material parameters for VHB 4910 identified by the developed material characterization package through data fitting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G^{EQ} )</td>
<td>12.9 kPa</td>
<td>( G_2^{NEQ} )</td>
<td>6.54 kPa</td>
<td>( G_4^{NEQ} )</td>
<td>21.51 kPa</td>
</tr>
<tr>
<td>( J_{\text{lim}} )</td>
<td>466.49</td>
<td>( \eta_{20} )</td>
<td>10.28 MPa ( \cdot ) s</td>
<td>( \eta_{40} )</td>
<td>276.12 kPa ( \cdot ) s</td>
</tr>
<tr>
<td>( G_1^{NEQ} )</td>
<td>0.47 kPa</td>
<td>( G_3^{NEQ} )</td>
<td>5.96 kPa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4-2 Material parameters for VHB 4910 identified by manual model configuration through data fitting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^{EQ}$</td>
<td>13.0 kPa</td>
<td>$G_2^{NEQ}$</td>
<td>8.49 kPa</td>
<td>$G_4^{NEQ}$</td>
<td>49.57 kPa</td>
</tr>
<tr>
<td>$J_{lim}$</td>
<td>471.96</td>
<td>$\eta_{20}$</td>
<td>10.0 MPa·s</td>
<td>$\eta_{40}$</td>
<td>103.9 kPa·s</td>
</tr>
<tr>
<td>$G_1^{NEQ}$</td>
<td>0.30 kPa</td>
<td>$G_3^{NEQ}$</td>
<td>9.98 kPa</td>
<td>$\eta_{10}$</td>
<td>75.88 MPa·s</td>
</tr>
<tr>
<td>$\eta_{30}$</td>
<td>1.42 MPa·s</td>
<td>$\eta_{30}$</td>
<td>1.0 MPa·s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After the equilibrium constitutive model is selected, the next step is to identify the non-equilibrium constitutive model and the corresponding non-equilibrium material parameters. This is realized by data fitting the theoretical nominal stress-stretch relation to the experimentally measured stress-stretch curves under different loading rates. Within the stretch range of $\lambda \in [1, 2]$, the experimental data [48] for a VHB 4910 specimen under a cyclic loading-unloading process with two different loading rates are used for this purpose. As there may exist $n$ different types of viscous subnetworks in the elastomer, for the non-equilibrium material parameter selecting, the number of the undetermined parameters is set as, $nvars=n^*(the\ total\ number\ of\ the\ non\-equilibrium\ material\ parameters\ of\ the\ six\ constitutive\ models)+5$ in the “ga” function, i.e., $nvars=25n+5$. As the first step, the lower bound $lb$ and the upper bound $ub$ of the non-equilibrium parameter vector $v^{NEQ}$ are manually set with a relatively wider range as the input of the “ga” function Eq. (3.57). Then the initial values of the non-equilibrium parameter vector $v^{NEQ}$ can thus be generated by the “ga” function, which is used to calculate the non-equilibrium nominal stress defined by Eq. (3.63) in the last Chapter. While the equilibrium nominal stress in Eq. (3.63) is calculated by using the selected equilibrium constitutive model, i.e., the Gent model, and the corresponding material parameters. These calculated nominal stresses from Eq. (3.63) and the experimental nominal stress of two loading paths according to different stretch
ratios are used to define the fitness function $func$ as one of the inputs for the “ga” function. The reason of choosing experimental data from two loading paths not a close loading-unloading cycle is to avoid the possible not-a-number (NAN) condition serving as the initial values of stretch ratios of the unloading path, which will lead to the abnormal termination of 'ga' function without any output. The NAN condition could occur due to the inappropriate parameters generated by the internal optimization process in the “ga” function. After all the inputs of the “ga” function are assigned, the “ga” function is run for optimization following the same procedure as selecting the equilibrium constitutive model to return the optimized output of the selected non-equilibrium constitutive model and the corresponding material parameters. It should be mentioned that the ‘ga’ function is run for optimization by increasing the number of the viscous subnetworks step by step. When the number of subnetworks $n$ is set as a small value, for example, when $n=1$ or 2, it is found that there is significant discrepancy between the theoretical nominal stress-stretch relation from the experimental curve. The selected constitutive model is regarded as invalid since one or two viscous subnetworks are not capable of capturing the stress relaxation accurately. Then we need to increase the number of the viscous subnetworks and keep running the “ga” function for optimization until an appropriate $n$ is selected. Once $n$ is fixed, the identification process for the non-equilibrium state is also repeated for the purpose of eliminating the effect of uncertainty until a small and acceptable $fval$ is obtained. Thus, the optimized non-equilibrium material parameters are identified, which are listed in Table 4-1 for the case of four viscous subnetworks. Again, the manual model configuration is also conducted by manually selecting the Gent model as the non-equilibrium constitutive model with 4 viscous subnetworks. The material parameters are identified by data fitting of the theoretical nominal stress-stretch relation to the experimental data as shown in Figure 4-2. These material parameters are listed in Table 4-2, which demonstrate a good agreement with the results of the material model selection from the constitutive database and the material parameter identification process. It is observed from these two Tables that both the equilibrium material parameters and the material viscosity at the undeformed state agree very well, while there is some discrepancy for the non-equilibrium shear modulus between these two data-fitting methods. It should be mentioned that the non-equilibrium
shear modulus is at much lower magnitude than the viscosity of the elastomer at the undeformed state.

Figure 4-1 Comparison of simulation results and experimental data under quasi-static loading condition for VHB 4910. (a) simulation results from the developed material characterization package; (b) simulation results from manual model configuration.
Figure 4-2 Comparison between simulation results and experimental data in a loading-unloading process with the maximum stretch ratio of 2 under different stretching rates. (a) simulation results from the developed material characterization package; (b) simulation results from the manual model configuration.

Figure 4-3 depicts the theoretical nominal stress-stretch curve determined from data-fitting material parameters in comparison with the experimental data under a cyclic loading-
unloading process with increasing the maximum stretch ratio up to $\lambda_{\text{max}} = 3$. These results validate the capability and feasibility of the developed material property characterization package. Regardless of the large discrepancy of the non-equilibrium shear modulus determined from the developed material characterization package and from the manual model configuration, the theoretical nominal stress-stretch curves are all in good agreement with the experimental data as shown in Figure 4-3(a) and Figure 4-3(b). It means that the macroscopic response of VHB 4910 may not be sensitive to the non-equilibrium shear modulus of the viscous subnetworks in the polymer.
Figure 4-3 Comparison between simulation results and experimental data in a loading-unloading process with the maximum stretch ratio of 3 under different stretching rates. (a) simulation results from the developed material characterization package; (b) simulation results from the manual model configuration.

To quantitively evaluate the data fitting between the theoretical simulation results and the experimental data, the coefficient of determination $R^2$ in the regression analysis and the relative error of the loading-unloading paths are demonstrated here when the elastomer is stretched to $\lambda_{\text{max}} = 2$ and $\lambda_{\text{max}} = 3$, respectively, with different loading rates. The coefficient of determination $R^2$ is a statistic concept that reflects the percentage of the data points falling into the curve that is formed by the regression equation on the global scale, which is calculated as,

$$R^2 = \frac{\sum_{m=1}^{M} \left[ \left( P_{\text{theoretical}} \right)_m - \bar{P}_{\text{experimental}} \right]^2}{\sum_{m=1}^{M} \left[ \left( P_{\text{experimental}} \right)_m - \bar{P}_{\text{experimental}} \right]^2} \quad (4.1)$$

where $\bar{P}_{\text{experimental}}$ is the mean value of the experimental nominal stress, $P_{\text{theoretical}}$ is the interpolated theoretical nominal stress in response to the experimental stretch ratio, $M$ is
the number of experimental data points. The $R^2$ value falls into the range of $[0,1]$ for the most cases. The higher the $R^2$ value, the better the model fits the real data, with $R^2 = 1$ representing a perfect data-fitting. The $R^2$ values for the data fitting under different loading-unloading processes are listed in Table 4-3. As observed in the table, the high values of $R^2$ indicate that the selected Gent model for both equilibrium and non-equilibrium states is capable of characterizing the viscoelastic response of VHB 4910.

<table>
<thead>
<tr>
<th>Configuration type</th>
<th>Material characterization package</th>
<th>Manual model configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$98.39%$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$99.02%$</td>
</tr>
</tbody>
</table>

The relative error of the points on the regression line to the experimental data when the elastomer is subjected a stretch up to $\lambda_{\text{max}} = 2$ under different loading rates is plotted in Figure 4-4. Figure 4-4(a) shows the relative error in the loading path, while Figure 4-4(b) depicts the relative error in the unloading path. As shown in Figure 4-4(a), the relative error between the experimental nominal stress and the interpolated theoretical simulation points decreases dramatically when the stretching starts to increase. For example, when the VHB 4910 specimen is elongated to $\lambda = 1.25 \times \lambda_{\text{max}}$, the relative error is lower than 10%. Afterwards, as the material is further stretched, the relative error continues to drop and then keeps blow 5%. In the unloading process, a small relative error is observed when the unloading process starts as shown in Figure 4-4(b). When the material is fully relaxed with zero nominal stress, the relative error is getting larger. The large relative error at the beginning of the loading path and at the end of the unloading path is due to the fact that when the nominal stress approaches to zero, any small variation of the theoretical nominal stress may cause a large relative error. Similar trend of the relative error between the theoretical calculated nominal stress and the experimentally measured nominal stress is observed when the VHB 4910 is under loading-unloading process with a stretch up to $\lambda_{\text{max}} = 3\times \lambda_{\text{max}}$. 

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Figure 4-4 Relative error between simulation results and experimental data on the loading and unloading paths of a uniaxial tension test with different stretching rates. (a) loading path with a maximum stretch ratio of 2; (b) unloading path with a maximum stretch ratio of 2; (c) loading path with a maximum stretch ratio of 3; (d) unloading path with a maximum stretch ratio of 3.
From the analysis of the coefficient of determination $R^2$ and the relative error of the data fitting, it is evident that the Gent model is suitable to characterize the viscoelastic behavior of VHB 4910, and the identified material parameters are reliable to predict the response of VHB 4910. Similar to the work performed by Zhou et al. [42], we will use the selected model to predict the viscoelastic response of VHB 4910 under a wider range of deformation and stretching rates. The nominal stress-stretch responses of the VHB 4910 specimen within the stretch interval of $\lambda \in \left[1, 9\right]$ are plotted in Figure 4-5 with various loading rates. At relatively low stretching rates (for example, 0.01/s, 0.03/s and 0.05/s), the loading and unloading curves overlap when the material is under relatively large deformation. This is caused by the relatively low viscosity $\eta_{B_n}$ of the viscous subnetwork $B_n$ at relatively large deformation, which allows the material to relax much faster. However, when the material is loaded under a relatively large stretch rate, e.g., 1/s, a wider gap between the loading and unloading curves is observed, resulting from insufficient time for the relaxation of the material during the deformation.

Figure 4-5 Viscoelastic response of VHB 4910 under a wider range of deformation with different loading rates
The variation of the nonlinear viscosity $\eta_{B_n}$ ($n=1,2,3,4$) of the four viscous subnetworks and the corresponding relaxation times $\tau_{B_n}$ ($\tau_{B_n} = \eta_{B_n}/G^{\text{NEQ}}_n$) with the uniaxial stretching of the material at a particular stretching rate of 0.05/s is illustrated in Figure 4-6. As shown in this figure, both the viscosity and the relaxation time of all the viscous subnetworks drops dramatically when the stretching starts, while the decrease of the viscosity becomes slowly when the stretch ratio reaches a relatively large value. The evolution of the material viscosity with the deformation can be used to explain the macroscopic response of the material as shown in Figure 4-5. The rapidly dropped viscosity allows the material to relax much faster, resulting in a fast decrease of the stress. It is reflected as the strain-softening behavior of the elastomer as shown in Figure 4-5, i.e., the nominal stress first increases with the stretch ratio, then appears to reach a plateau while sustaining further stretching. With further increasing of the stretch ratio, the stress shows a remarkable increase in response to the increasing stretch, which is the typical strain-hardening behavior of the material.
4.2 Material property characterization for HNBR50

Another commonly used elastomer HNBR50 is also considered to test the capability of the developed material characterization package. The identification of the equilibrium and the non-equilibrium material parameters follows the same procedure as that of VHB 4910. Similarly, we will use the experimental data from the quasi-static loading condition for selecting the equilibrium constitutive model and identifying the corresponding equilibrium parameters. In this case, the equilibrium nominal stress data of HNBR50 [38] plotted in Figure 4-7 were obtained at the end of a relaxation period of 2h. As the nominal stress at the same stretch is observed to have identical values on both the loading and unloading paths at the end of the long relaxation time, implying the same effect of the quasi-static loading condition. For the identification of equilibrium material parameters, all the inputs of ‘ga’ function defined by Eq. (3.57) in the last Chapter should be assigned in advance. The number of the undetermined parameters is set as nvars = 22, which is the total number of the equilibrium parameters of the six constitutive models plus 5. The lower bound lb and the upper bound ub of the equilibrium parameter vector $v^E$ with a manually set wider
range serve as the initial inputs of the ‘ga’ function. The fitness function \textit{func} defined by
Eq. (3.58) is determined from the experimental nominal stress and theoretical nominal
stress calculated by the initial values of the equilibrium parameter vector \( \mathbf{v}^{EQ} \), which is a
random parameter set generated by ‘ga’ function based on the upper bound \( \mathbf{ub} \) and the
lower bound \( \mathbf{lb} \). With all the inputs, the ‘ga’ function is run for iterative optimization and
then return the determined parameter vector \( \mathbf{v}^{EQ} \), providing the selected equilibrium
constitutive model and corresponding equilibrium parameters. This optimization process
is conducted repeatedly until a small or acceptable \textit{fval}, namely the RMSE between
theoretical results and the experimental data, is observed among the several times of
calculations, indicating a good quality of data fitting. In the end, the non-affine model is
identified as the most suitable equilibrium constitutive model and the corresponding
material parameters \( G_{c}^{EQ} \), \( G_{e}^{EQ} \) and \( \lambda_{\text{max}} \) are obtained as listed in Table 4-4. An excellent
agreement between the data fitting of the theoretical stress-stretch curve and the quasi-
static experimental data is demonstrated in Figure 4-7.

\textbf{Table 4-4 Material parameters for \textit{HNBR 50} identified by the developed material characterization package}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{c}^{EQ} )</td>
<td>82.16 kPa</td>
<td>( \eta_{10} )</td>
<td>254.1 MPa·s</td>
<td>( G_{4}^{NEQ} )</td>
<td>161.81 kPa</td>
</tr>
<tr>
<td>( G_{e}^{EQ} )</td>
<td>217 kPa</td>
<td>( G_{2}^{NEQ} )</td>
<td>106.6 kPa</td>
<td>( \eta_{40} )</td>
<td>2.92 MPa·s</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>2.439</td>
<td>( \eta_{20} )</td>
<td>9.518 GPa·s</td>
<td>( G_{3}^{NEQ} )</td>
<td>47.72 kPa</td>
</tr>
<tr>
<td>( J_{\text{lim}} )</td>
<td>14.84</td>
<td>( G_{1}^{NEQ} )</td>
<td>98.08 kPa</td>
<td>( \eta_{30} )</td>
<td>1.023 MPa·s</td>
</tr>
<tr>
<td>( G_{1}^{NEQ} )</td>
<td>98.08 kPa</td>
<td>( \eta_{30} )</td>
<td>1.023 MPa·s</td>
<td>( G_{3}^{NEQ} )</td>
<td>47.72 kPa</td>
</tr>
</tbody>
</table>

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In the following, we will determine the non-equilibrium constitutive model and the corresponding material parameters with the selected non-affine model as the equilibrium constitutive model. The identification process is performed by fitting the theoretical nominal stress-stretch relation to the experimental stress-stretch curves obtained from cyclic tension-compression tests under different loading rates within the stretch range of \( \lambda \in [0.75, 2] \) [38]. Considering \( n \) different types of non-equilibrium subnetworks, the input \( nvars \) of the “ga” function is set as \( nvars=25n+5 \). Accordingly, the input of the lower bound \( lb \) and the upper bound \( ub \) of the non-equilibrium parameter vector \( v^{NEQ} \) is set within a wider range at the first step. The initial guess of the non-equilibrium parameter vector \( v^{NEQ} \) is randomly generated by the ‘ga’ function according to the assigned lower and upper bounds, which are used to calculate the non-equilibrium nominal stress defined by Eq. (3.63) in the last Chapter. While the equilibrium nominal stress in Eq. (3.63) is calculated by using the determined non-affine model and the corresponding material parameters. Then the calculated nominal stress, combined with the experimental nominal stress on the first
loading path with the loading rate of 5/min and 0.5/min, are used to determine the fitness function \( \text{func} \) as the input of the ‘ga’ function. Following the same optimization procedure as outlined for VHB4910, four viscous subnetworks are determined as the appropriate number of the viscous subnetwork and the Gent model is identified as the non-equilibrium constitutive model. The corresponding non-equilibrium material parameters describing the Gent model are listed in Table 4. Using the determined equilibrium and non-equilibrium constitutive models, the theoretical nominal stresses on the unloading path and the second loading-unloading path when the specimen under the same loading rate, i.e., \( |\dot{\varepsilon}| = 5/\text{min} \) and \( |\dot{\varepsilon}| = 0.5/\text{min} \) are determined. Then the complete nominal stress-stretch curves in the tension-compression process are plotted in Figure 4-8 and Figure 4-9 for these two different loading rates, demonstrating a good agreement with the experimental data. Figure 4-10 illustrates the theoretical nominal stress-stretch curves and the experimental data of a cyclic tension-compression with the stretching rate of \( |\dot{\varepsilon}| = 0.05/\text{min} \) as a validation for the selected constitutive models at both the equilibrium and non-equilibrium states. Similar to the findings of Zhou et al. [42], the data fitting quality for HNBR50 is not as satisfactory as that for VHB 4910 as demonstrated in Figure 4-8 and Figure 4-9. It was argued by Zhou et al. [42] that it may be caused by the pre-damaging treatment on the HNBR50 specimen before the cyclic tension-compression tests for the purpose of excluding the Mullins softening effect [34, 36, 38, 105] from the viscoelastic behaviors.
Figure 4-8 Comparison between experimental data under 5/min and simulation results

Figure 4-9 Comparison between experimental data under 0.5/min and simulation results
The coefficient of determination $R^2$ values for the loading process of the tension-compression tests under different loading rates are listed in Table 5, indicating acceptable data fitting results.

<table>
<thead>
<tr>
<th>Loading rate</th>
<th>5/min</th>
<th>0.5/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>92.91 %</td>
<td>95.59 %</td>
</tr>
</tbody>
</table>

The relative error of each data point on the regression line to the experimental data on the tension-compression-tension loading paths under three stretching rates is plotted in Figure 4-11. Figure 4-11(a), (b) and (c) represent the relative error of the data points on the first tension path with $\lambda \in [1, 2]$, the compression path with $\lambda \in [2, 0.75]$ and the second tension path with $\lambda \in [0.75, 2]$, respectively. As observed in Figure 4-11(a), the relative error shows a descending trend with the increase of the stretch ratio, i.e., under 10% when the stretch reaches $\lambda = 1.6$ and maintaining around 5% with further increasing of the stretch.
ratio. In the compression process shown in Figure 4-11(b), the relative error is relatively small from the beginning of the compression. Once the material is fully relaxed with zero nominal stress, the relative error becomes larger, otherwise will keep within a reasonable range. In the second tension loading process starting from $\lambda_{\text{min}} = 0.75$ as shown in Figure 4-11(c), the relatively large error occurs when the nominal stress approaches to zero. Again, the large relative error of the data fitting on the tension-compression-tension paths is due to the fact that any small variation of the theoretical nominal stress may cause a large relative error when the nominal stress is approaching to zero.
Figure 4-11 Relative error between simulation results and experimental data under a cyclic tension-compression process with different stretching rates. (a) the first tension process up to a stretch ratio of 2; (b) compression process with stretch ratio decreasing to 0.75; (c) the second tension process a stretch ratio up to 2.
The selected constitutive models and the determined material parameters are further utilized to simulate the cyclic tension-compression test with 12 one-hour relaxation intervals under the strain rate of $|\dot{\lambda}| = 3/\text{min}$ (Miehe and Göktepe, 2005), aiming to investigate the relaxation behavior. The one-hour relaxation was performed at the stretch of $\lambda = 0.75, 0.875, 1, 1.25, 1.5, 1.75$ and $2$, respectively, on both the tension and compression paths. The experimental data and corresponding simulation results are plotted in Figure 4-12. It is observed in this figure that the selected constitutive models are capable of capturing the stress-stretch response under complex loading conditions. Another simulation is also performed to predict the response of the material when subjected to large deformation up to $\lambda_{\text{max}} = 4$ under different stretching rates of $0.01/\text{min}$, $0.05/\text{min}$, $0.1/\text{min}$, and $1/\text{min}$, respectively. As observed in Figure 4-13, the loading and unloading paths overlap when the material is subject to large deformation which is attributed to the small material viscosity. Also, the rate-dependent responses are observed, i.e., the larger stress is induced by the higher stretching rate. The variation of the nonlinear viscosity $\eta_{B_n}$ of the four viscous subnetworks and corresponding relaxation time $\tau_{B_n}$ at the strain rate of $\dot{\lambda} = 0.1/\text{min}$ is shown in Figure 4-14. Both the viscosity and the relaxation drop rapidly at the beginning of deformation and reaches a small value when the elastomer is subjected to large deformation. This can be used to explain the overlapping of the loading and unloading paths in Figure 4-13 when the elastomer undergoes large deformation, i.e., the small viscosity allows the fast relaxation. From the results, it is concluded that the developed material characterization package is capable of characterizing material properties for providing good prediction of the viscoelastic responses of the elastomer under complex tension-compression loading.
Figure 4-12 Comparison between simulation results and experimental data from cyclic tension-compression tests with one-hour relaxation intervals.

Figure 4-13 Prediction of stress responses under large deformation with different stretching rates.
Figure 4.14 Variation of material viscosity $\eta_{B_n}$ and relaxation time $\tau_{B_n}$ of four viscous subnetworks of HNBR50 at a stretching rate of 0.1/m. (a) subnetwork $B_1$; (b) subnetwork $B_2$; (c) subnetwork $B_3$; (d) subnetwork $B_4$. 
4.3 Material property characterization for carbon black (CB) filled rubber

It is well adopted in the literature that particle-reinforced rubbers exhibit distinctive viscoelastic behavior from unfilled rubbers [51, 105]. To further validate the developed material property characterization package, carbon black (CB) filled rubber is taken as another example for constitutive model selection and material parameter identification. Successive loading-unloading test at a stretch rate of 0.02/s was performed on the CB filled rubber specimen to capture the Mullins’ softening behavior [50], the experimental stress-stretch data is plotted in Figure 4-15. Unlike VHB 4910 and HNBR50, there is a lack of experimental data obtained for CB filled rubbers under quasi-static loading condition in the literature. Consequently, the equilibrium and non-equilibrium constitutive models as well as the corresponding material parameters will be determined simultaneously by fitting the theoretical nominal stress-stretch curves to the experimental data. Therefore, the individual settings of the ‘ga’ function should be adjusted to accommodate the total 36 model configurations (6 for the equilibrium constitutive models and 6 for the non-equilibrium constitutive models). The parameter vector $\mathbf{v}$ is assigned as a combination of the equilibrium parameter vector $\mathbf{v}^{EQ}$ of Eq. (3.60a) and the non-equilibrium parameter vector $\mathbf{v}^{NEQ}$ of Eq. (3.60b), as,

$$
\mathbf{v} = \begin{bmatrix}
C_{10}^{EQ} & C_{20}^{EQ} & C_{30}^{EQ} & G_{10}^{EQ} & G_{01}^{EQ} & G_{lim}^{EQ} & G_{c}^{EQ} & G_{c}^{EQ} & \lambda_{max}^{EQ} \\
C_{10}^{NEQ} & C_{20}^{NEQ} & C_{30}^{NEQ} & G_{10}^{NEQ} & G_{01}^{NEQ} & \eta_{c}^{NEQ} & \mu_{1}^{NEQ} & \mu_{2}^{NEQ} & \mu_{3}^{NEQ} \\
\mu_{1}^{EQ} & \mu_{2}^{EQ} & \mu_{3}^{EQ} & \alpha_{1}^{EQ} & \alpha_{2}^{EQ} & \alpha_{3}^{EQ} & \alpha_{4}^{EQ} & \alpha_{5}^{EQ} & x, y, z, a, b \\
\eta_{c}^{EQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} \\
\eta_{c}^{EQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} & \eta_{c}^{NEQ} \\
x', y', z', a', b' 
\end{bmatrix}
$$

(4.2)

Thus, the number of to-be-determined parameters $n\text{var}$ in the ‘ga’ function of Eq. (3.57), is set as the total number of both the equilibrium and the nonequilibrium material parameters of the six constitutive models as listed in Table 3-2 plus 10 (the number of the
two model selection parameter sets), i.e., \( n_{\text{var}}=25n+27 \). The theoretical nominal stress in the fitness function \( \text{func} \) is adjusted by the weighted summation of both the equilibrium and the non-equilibrium nominal stresses of different constitutive models, i.e.,

\[
P_{\text{theoretical}} = p^* (P_{\text{EQ}})_{\text{sil}} + q^* (P_{\text{EQ}})_{\text{v}} + r^* (P_{\text{EQ}})_{\text{MR}} + s^* (P_{\text{EQ}})_{\text{G}} + t^* (P_{\text{EQ}})_{\text{NA}} + u^* (P_{\text{EQ}})_{\text{O}}
\]

(4.3)

\[
\begin{align*}
&+ p^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{sil}} (F_{\text{B}}^{i})^{-1} + q^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{v}} (F_{\text{B}}^{i})^{-1} + r^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{MR}} (F_{\text{B}}^{i})^{-1} \\
&+ s^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{G}} (F_{\text{B}}^{i})^{-1} + t^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{NA}} (F_{\text{B}}^{i})^{-1} + u^* \sum_{n=1}^{N} (P_{\text{NEQ}}^E)_{\text{O}} (F_{\text{B}}^{i})^{-1}
\end{align*}
\]

The weighting coefficient set \( [p,q,r,s,t,u] \) is associated with the equilibrium constitutive models, and the values are controlled by the parameter set \( [x,y,z,a,b] \) following the relationship of Eq. (3.62). While the weighting coefficient set \( [p',q',r',s',t',u'] \) for the viscous subnetworks is associated with the non-equilibrium constitutive models, controlled by the parameter set \( [x',y',z',a',b'] \). At the first step, the lower bound \( lb \) and the upper bound \( ub \) of the parameter vector \( v \) are manually set with a relative wider range as one of the inputs. Then the initial values of the parameter vector \( v \) are generated randomly by the ‘ga’ function, which are further used to calculate the total theoretical nominal stress according to Eq. (4.3). The calculated nominal stresses and the nominal stresses measured from the first loading path in the experiment [51] are used to make up the fitness function \( \text{func} \). After all the inputs of the ‘ga’ function are well adjusted and assigned, the ‘ga’ function is run for internal optimization to obtain the parameter vector, which outputs the selected equilibrium and non-equilibrium constitutive models and the corresponding material parameters. Following the same optimization procedure as described for VHB 4910 and HNBR50 by increasing the number of the viscous subnetworks as well as narrowing the range of the lower bound \( lb \) and the upper bound \( ub \), it is read from the determined parameter vector \( v \) that three subnetworks are sufficient to characterize the viscous behavior of the CB filled rubber, and the Gent model is selected as the equilibrium constitutive model while the Ogden model is identified as the non-equilibrium model. The determined material parameters in accordance with the Gent model and the Ogden model are listed in Table 4-6, which are used to calculate the theoretical nominal stresses in
response to the stretch in the first unloading and the second loading-unloading processes. The complete theoretical stress-stretch curves of the first and second loading-unloading processes are also depicted in Figure 4-15 for comparison purpose, demonstrating a good fitting quality to the experimental data from the first loading-unloading process. The coefficient of determination $R^2$ value for the first loading process at a stretching rate of 0.02/s is determined as 99.23%. The theoretical nominal stress-stretch curve of the second loading-unloading process with the corresponding experimental data serves as a validation for the determined model configuration and the identified material parameters.

Table 4-6 Material parameters for CB filled rubber identified by the developed material characterization package

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G^{EQ}$</td>
<td>0.169 MPa</td>
<td>$\eta_{10}$</td>
<td>717.83 MPa•s</td>
<td>$\mu_{i3}$</td>
<td>-0.656 MPa</td>
</tr>
<tr>
<td>$J_{lim}$</td>
<td>10.58</td>
<td>$\mu_{12}$</td>
<td>-0.059 MPa</td>
<td>$\mu_{23}$</td>
<td>0.538 MPa</td>
</tr>
<tr>
<td>$\mu_{11}$</td>
<td>-0.423 MPa</td>
<td>$\mu_{22}$</td>
<td>0.649 MPa</td>
<td>$\mu_{33}$</td>
<td>-0.965 MPa</td>
</tr>
<tr>
<td>$\mu_{21}$</td>
<td>0.57 kPa</td>
<td>$\mu_{32}$</td>
<td>-0.406 MPa</td>
<td>$\alpha_{13}$</td>
<td>-0.040</td>
</tr>
<tr>
<td>$\mu_{31}$</td>
<td>0.667 MPa</td>
<td>$\alpha_{12}$</td>
<td>-0.0712</td>
<td>$\alpha_{23}$</td>
<td>0.344</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>-0.472</td>
<td>$\alpha_{22}$</td>
<td>0.604808</td>
<td>$\alpha_{33}$</td>
<td>-0.0015</td>
</tr>
<tr>
<td>$\alpha_{21}$</td>
<td>9.31</td>
<td>$\alpha_{32}$</td>
<td>-0.08643</td>
<td>$\eta_{30}$</td>
<td>242.86 MPa•s</td>
</tr>
<tr>
<td>$\alpha_{31}$</td>
<td>0.628</td>
<td>$\eta_{20}$</td>
<td>364.91 MPa•s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relative error of each data point of the theoretical stress-stretch curves to the experimental data in the loading-unloading cycles is plotted in Figure 4-16. As shown in Figure 4-16, the relative error of each loading or unloading path decreases at first, and then fluctuates around 10% with the increase of the stretch ratio. For the first loading path, the relative error drops rapidly, and then maintains within 5% with the further increase of the stretch ratio, which demonstrates an excellent data fitting between the theoretical results and the experimental data. For the first unloading path, the relative error is not as satisfactory as that of the first loading path since the relative error at the range of $\lambda \in [2.2, 2.8]$ is above 10%, while the maximum value is still smaller than 20%. Except for the relatively large error when nominal stress approaches zero, in general the theoretical nominal stress-stretch curve calculated from the selected constitutive models agree well with the experimental data for both the loading and unloading paths.
The determined constitutive models and the corresponding material parameters are further used to predict the stress response of carbon black (CB) filled rubber with different stretch rates of 0.02/s, 0.05/s, and 0.1/s, respectively. As observed in Figure 4-17, the Mullins’ effect along with the rate-dependent viscoelastic behavior is well captured. The Mullins’ effect can be interpreted by the evolution of the inelastic stretch ratios as illustrated in Figure 4-18. During the first loading-unloading cycle, the inelastic stretch ratios of the three viscous subnetworks keep increasing to a relatively large value, resulting in a smaller elastic stretch in the second loading process than that in the first loading path. Therefore, the elastic stress of the second loading path becomes smaller aiming at the same total stretch.
Figure 4-17 Stress response of CB filled rubber under different stretch loading rates.

Figure 4-18 Inelastic stretch evolution in the CB filled elastomer sample during the first loading-unloading cycle with a loading rate of 0.05/s.
It is justified from these case studies that the developed material property characterization package has demonstrated strong capability of characterizing the typical viscoelastic behavior of elastomeric materials. As the developed material characterization package is capable of adopting most strain energy density functions for hyperelasticity and the thermodynamics evolution laws for viscoelastic materials, it is expected to provide a general platform for characterizing viscoelastic properties of new elastomeric materials whenever experimental data are available.
Chapter 5

5 Conclusion and Recommendations for Future Work

5.1 Conclusions

Elastomeric materials have applications in various industrial fields due to their intrinsic hyperelasticity and viscoelasticity. In order to fulfill the potential applications of elastomers, particularly for new-designed elastomers, it is crucial to characterize the material properties that can quantitatively represent their viscoelastic behavior. In the current work, a material property characterization package is thus developed to select appropriate constitutive models and identify the relevant material parameters. To the end, the contributions of the current work are summarized as follows:

1. A material property characterization package, which consists of a constitutive model database and the corresponding selection strategy. The constitutive model database is composed of formulations of various constitutive models, which are derived based the continuum mechanics framework incorporated with the nonlinear material viscosity.
2. The capability and feasibility of the developed material property characterization package is validated by three commonly used elastomers, including both filled and unfilled rubbers. The selected material models and the corresponding material parameters can be used to capture the typical hyperelastic and viscoelastic behavior of elastomers under different loading conditions
3. The material property characterization package is capable of quantifying the representative material parameters of various elastomers.
4. This thesis work is expected to establish a general platform for material property characterization.
5.2 Future work

Based on the current work, some suggestions on the further development of the material characterization package are given as below:

1. The constitutive model database of the material characterization package exhibits high flexibility of adding more constitutive models. Other constitutive models can be formulated based on the continuum mechanics framework to enrich the model database, which will enable the developed package to provide material property characterization for a wider range of elastomeric materials. In addition, multiphysics coupling can also be incorporated into this general platform for material property characterization.

2. The material characterization package can be further incorporated with the machine learning. Machine learning is a method that improve the computing algorithm through experience and known data [106]. The material property characterization package can be used to create a material response database as the training data, which consists of the microstructure, the constitutive model and the corresponding material properties, and the material responses under different loading conditions [107]. Then the machine learning can be applied to the material response database to obtain a new design or new model, which can further be used to investigate the impact of the microstructure on the properties or the design of new elastomers by tailoring the microstructure of elastomers.
References


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