I, Nepolean Rajasekaran, hereby submit this original work as part of the requirements for the degree of Master of Science in Mechanical Engineering.

It is entitled: 

A Nonlinear Constitutive Model for High Density Polyethylene at High Temperature

Student's name: Nepolean Rajasekaran

This work and its defense approved by:

Committee chair: Dong Qian, PhD

Committee member: Jim Shepherd, PhD

Committee member: Yijun Liu, PhD
A Nonlinear Constitutive Model for High-Density Polyethylene at High Temperature

A thesis submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of Master of Science in the School of Dynamic Systems of the College of Engineering & Applied Science January 2011

by Nepolean Rajasekaran Bachelor of Engineering PSG College of Technology, Coimbatore, India May 2005

Committee Chair: Dr. Dong Qian
ABSTRACT

High density polyethylene (HDPE) is a common polymer material that is widely used in industrial applications. While significant amount of efforts have been devoted to understanding the constitutive behavior of HDPE, very little work has been performed to investigate the material response of HDPE at high strain rate and high temperature. The main objective of this research is to develop a constitutive model to bridge this gap by focusing on the non-linear stress-strain behavior in the high strain rate and high temperature range. A series of monotonic uniaxial compressive tests have been conducted at high temperature (100°C) and high strain rate (1/s) to characterize the HDPE behavior. Based on the experimental results, existing hyperelastic material models such as Mooney-Rivlin, Ogden, Arruda-Boyce, are assessed with the use of ABAQUS (a finite element software). Based on extensive comparisons, a new three-dimensional constitutive model for HDPE has been proposed. The constitutive equation integrates the basic mechanisms proposed by Boyce et al. [6] and Shepherd et al. [8]. The total stress is decomposed into an elastic-viscoplastic representation of the intermolecular resistance acting in parallel with a time and temperature dependent network resistance of polymer chains. Material constants involved in the model were calculated by fitting the compressive test results to the proposed constitutive equations. A constitutive solver for the proposed model has been developed. The stress-strain relation resolved from the constitutive model closely matches the corresponding ones from the experiments.
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Chapter 1

Introduction

1.1 Background and motivation

Polymers are materials consisting long molecular chains made up of many repeating small molecules (called monomers) linked by chemical bonds. One such an example is polyethylene in which ethylene is the monomer. A variety of polymers can be found in use and they generally fall under two major categories: natural and synthetic polymers. For example, natural polymers include cellulose, natural rubber, etc. On the other hand, neoprene, bakelite and nylon are the examples of synthetic polymers.

In modern world, polymers are used in applications such as aerospace, automobile, fluid transport, electronics and food processing industries. These polymer products are mostly manufactured by processes such as injection stretch blow molding (used for polyethylene terephthalate), extrusion blow molding (used for high density polyethylene), etc., which are often sequential and non-isothermal stretching processes. When subjected to different loading conditions, polymers such as high density polyethylene (HDPE) exhibit a highly nonlinear stress-strain behavior depending on external factors (such as strain rate, temperature) and structural parameters (such as crystallinity degree, molecular weight and cross-linking)[14].

Boyce et al. [6] states that “Owing to the complexities of the dependencies of the material behavior and the manufacturing process itself, it is difficult to experimentally isolate and
determine the magnitude of the effects that small variations in different processing parameters can have on the end product”. Hence mechanical design of products made from these polymers proves to be an engineering challenge as far as prediction of deformation behavior is concerned. As it is generally expensive to perform extensive test and conduct accurate measurements, a numerical tool able to describe the polymer behavior is highly desired.

Taking advantage of the modern day high-speed computing and simulation techniques, modeling of the polymer manufacturing process using the finite element method could provide useful feedback about the variables involved during the design process. To execute such design studies, empirical constitutive model that can describe the polymer behavior needs to be in place first. Subsequently, the basic characteristic of the model is studied by developing a constitutive solver. Comparisons with other model predictions and experimental results are performed to test the validity of the model assumption. Finally a set of optimized model parameters are identified and the constitutive solver is integrated with the FEM simulation to make the prediction. The details on following this workflow are outlined in the later sections with a focus on HDPE.

In order to fully describe the thesis work, we first present some backgrounds that are relevant to this application in the next few sections.

1.2 Finite element (FE) method

FE method is a widely used numerical technique to solve/analyze problems in the field of solid mechanics. Generally, a continuum is discretized into a mesh of small parts (finite elements) connected by nodes and then loads/boundary conditions are applied on the resulting mesh. This model is then converted into a mathematical problem consisting of a set of simultaneous algebraic equations, whose solution gives the desired field quantities (displacement, load, etc) at
the nodes. An FE model typically yields piecewise continuous solutions. To determine the field quantities between the elements, shape functions are employed. For details on FEM, we refer to the work of Cook (1989) [32].

In the case of static equilibrium, the stiffness equation is solved in FEM and is expressed as

\[ [K]\{d\} = \{f\} \]  (1.1)

where \([K]\) is the so-called stiffness matrix, \(\{d\}\) is the nodal displacement vector due to the application of external forces \(\{f\}\).

1.3 Constitutive model

Constitutive model generally relates the stress in the material to inputs such as strain, strain rate, temperature, etc. For example, Hooke’s law is the simplest of all constitutive models which relates stress and strain of a linear elastic material. In 1D version, it reads as

\[ \sigma = E \varepsilon \]  (1.2)

where \(\sigma\) is the stress, \(\varepsilon\) is the strain and \(E\) is the modulus of elasticity (material constant).

In structural analysis, the response of the material is characterized by a constitutive equation which gives the stress as a function of the deformation history of the body. Different constitutive relations allow us to distinguish between different materials. For example, a viscous fluid and steel will have different constitutive models.

Polymer mechanics is very complex and various assumptions are made while developing a constitutive equation for polymers. It is generally infeasible to derive a universal constitutive model that would accurately represent the polymer behavior under different loading conditions. For example, hardening may occur in polymers under high strains or large loads, while this may
not be the case under small strains or small loads. With all other conditions being constant, different stress-strain behavior may be noticed under different loading rates. Hence, the constitutive model that is developed for polymer is often limited to specific conditions of interest such as particular ranges of strain, stress, loading rate and temperature. This treatment makes it easier to identify the model parameters by comparing with the experiment.

1.4 Objectives

As mentioned earlier, polymers exhibit different stress-strain behavior at different strain level and different temperatures. Based on strain range of interest, the constitutive equations used to model polymers can be classified into small and finite (large) deformation theories. For polymer, finite deformation theories need to be used due to the large deformation that is involved. If the polymer is processed at temperatures well above room temperature, temperature can have a significant effect and also needs to be incorporated in the constitutive model development.

In the manufacturing of a variety of plastic products such as milk bottles and detergent bottles, high density polyethylene is commonly used and undergoes large deformation when processed under high strain rate and high temperature. This is due to the combination of low cost and excellent mechanical properties. In addition, most of the HDPE can be recycled so that the environmental impact can be minimized [25].

Various material models based on small and large deformation theories predicting the deformation of HDPE at room temperature was developed over the last couple of decades. But there has been little work investigating finite deformation of HDPE at high strain rate and high temperature. Motivated by this critical knowledge gap, this thesis focuses on developing a
constitutive model to describe this complex behavior of HDPE at high strain rate and high temperature and compare it with experimental results.

To summarize, the objectives of this thesis are to

1. Conduct experiment and investigate the monotonic uniaxial compressive behavior of HDPE at high temperature (100°C) under high strain rate (1/s).
2. Evaluate the existing constitutive models by comparing with the experiment and assess the feasibility in describing the material behavior of HDPE.
3. Develop a new constitutive model for HDPE and identify the material constants based on experiment.
4. Validate the developed constitutive model with the experimental results.

1.5 Thesis structure

The rest of the thesis is organized as follows: In Chapter 2, the background related to constitutive models and basic principles which will be used in development of the new model are reviewed. Chapter 3 discusses the monotonic uniaxial compressive testing for characterizing HDPE at high temperature and high strain rate. In Chapter 4, existing hyperelastic material models are evaluated by comparing the model predictions with the experimental results. The formulation of new constitutive model for HDPE and the parameters involved are discussed in detail in Chapter 5. Chapter 6 presents the stress-strain results of the new model and comparison with the experimental results. In addition, the improvements made to the model after analyzing initial comparisons are discussed. Chapter 7 concludes the thesis and lists the possibilities of future work.
Chapter 2

Literature review

There is a continuing interest in the applications of polymers in various fields. In order to achieve optimized use of polymer resources, we need better understanding of their material behaviors and develop material models which can aid in their design. In this chapter, first a few elementary ideas about polymer structure and their properties are presented based on Ward (1983) [20]. This is followed by a review on the theories and constitutive models used for describing these properties.

2.1 Polymer structure

A Polymer is made up of long molecular chains of covalently bonded atoms. For example, polyethylene is made up of long chains of the \(-\text{CH}_2\) repeating unit. By addition polymerization of the monomer ethylene, \(\text{CH}_2 = \text{CH}_2\), polyethylene is formed. Polyethylene is denoted as \([-\text{CH}_2 - \text{CH}_2 -]_n\).

Mechanical properties of polymers are strongly influenced by their microstructure through cross-linking or chain-branching. For example, vulcanization of rubber, producing low or high density polyethylene. The long molecular chains are joined by other molecules or chains at some locations along their length to make a cross-linked structure (see Fig 2.1(d)). In case of chain-branching, a secondary chain originates from some locations on the main molecular chain (see Fig 2.1(e)).
Figure 2.1. Polyethylene: (a) polymerization, (b) linear HDPE, (c) skeletal form of HDPE, (d) cross linking, (e) chain branching (LDPE) [20].
2.2 Polymer properties

The first and foremost requirement in order to develop a constitutive model for polymer is the understanding of the mechanical behavior of polymers which we intend to capture in the model. Polymers exhibit different behaviors based on the operating conditions such as loading rate, temperature, and strain range. Due to this dependency of their mechanical behaviors on different testing conditions, categorization of polymers as a particular type of material such as glassy solid, viscous liquid or rubber is not possible. Hence, polymers are generally considered to be viscoelastic materials, as they exhibit properties which are intermediate to both viscous liquids and elastic solids.

Based on several experimental and literature studies, five basic characteristics have been identified in Ward (1983) [20], by which a polymer’s mechanical behavior can be differentiated from that of an ideal elastic solid obeying Hooke’s law. The five basic characteristics are:

1) behavior at large strains (finite elasticity and rubber-like/hyperelastic behavior)
2) time-dependent behavior (viscoelastic/viscoplastic behavior)
3) nonlinearity (nonlinear viscoelastic/viscoplastic behavior)
4) the behavior of oriented polymers (mechanical anisotropy)
5) the non-recoverable behavior (plasticity and yield)

Detailed explanation of properties and constitutive model used to capture them are explained in next few sections of this chapter.
2.3 Polymer modeling methods

There are several different approaches in developing constitutive models for polymers. All these models can be mainly categorized under two approaches:

(a) Micro-mechanical (or) physics-based model

(b) Macro-mechanical (or) phenomenologically-based model

Micro-mechanical models are based on the physics of the deformation. Therefore, any change in the deformation due to temperature and micro structure variation can be captured. The Macro-mechanical approach is based on using the invariants of stress or strain in the constitutive relation. Examples of micro-mechanical models are models such as Arruda-Boyce (1993) [5], Wu and van der Giessen (1993) [29], Shepherd et al. (2006) [8] and examples of macro-mechanical models are Mooney (1940) [30], Rivlin (1948) [31], Ogden (1972) [3].

2.4 Hyperelasticity

Finite elasticity and rubber-like behavior of polymers are best captured by hyperelastic material models which are generally phenomenologically-based models. Hyperelasticity deals with behavior of nonlinear elastic materials undergoing finite deformation. The stress in a hyperelastic material is calculated not directly from strain (like small strain, linear elastic materials), but from the principle of virtual work using the strain energy potential function $\Psi$ (Helmholtz free-energy function based on strain tensor). The strain energy potential function is expressed as principal invariants of deformation gradient tensor $F$ (i.e. invariants of either left or right Cauchy green deformation tensor). Specific definition of these concepts will be described next.
2.4.1 Basics of continuum mechanics

We consider the deformation of a general continuum. To describe such deformation, we introduce the material coordinate \( X \) and the spatial coordinate \( x \). The two are related through \( x = X + u \), in which \( u \) is the displacement. For detailed descriptions, we refer to standard reference on continuum mechanics [1].

![Displacement field of a particle in a general continuum](image).

**Figure 2.2. Displacement field of a particle in a general continuum.**

The deformation gradient tensor \( F \) relates quantities before and after deformations and is defined as,

\[
F = \frac{\partial x}{\partial X}
\]  
(2.1)

and

\[
J = \det(F)
\]  
(2.2)
where J is the determinant of $F$, known as the volume ratio or Jacobian determinant.

The deformation gradient tensor can be decomposed into stretch and rotation components,

$$ F = R \, U = V \, R $$

(2.3)

where $R$ is a unique orthogonal rotation tensor, $U$ and $V$ are unique, positive definite, symmetric tensors called as right and left stretch tensors, respectively.

Since the stretch tensors are evaluated from the polar decomposition, which are not simple to evaluate, the stretch tensors are not preferred measures of the deformation. Instead, the right and left Cauchy-Green strain tensors ($C$ and $B$) are often preferred as they are easier to evaluate. They are defined as,

$$ C = F^T F = U^2 \quad \text{and} \quad B = F F^T = V^2 $$

(2.4)

It is noted that $C$ and $B$ are symmetric and positive definite tensors.

With the definition of the Cauchy-Green strain tensor, the Lagrangian strain tensor ($E$) is given by

$$ E = \frac{1}{2} (C - I) $$

(2.5)

where $I$ is the identity tensor.

**2.4.2 Strain energy potential functions**

In the theory of a hyperelasticity, the actual work done by the stresses during a certain time interval (the deformation process) depends only on its initial and final time configuration ($t_0$ and $t$). Hence hyperelastic materials can also be categorized as path-independent materials.
Strain energy potential function $\Psi$ can be expressed as:

$$\Psi = \int_0^t \mathbf{S} : \dot{\mathbf{E}} \, dt \quad \text{and} \quad \Psi = \mathbf{S} : \dot{\mathbf{E}}$$ \hspace{1cm} (2.6)

where $\mathbf{S}$ is the second Piola-Kirchoff stress tensor, $\dot{\mathbf{E}}$ is the material derivative of the Lagrangian strain tensor.

Assume that $\Psi = \Psi(\mathbf{E}(\mathbf{X}), \mathbf{X})$, then,

$$\Psi = \sum_{i,j=1}^{3} \frac{\partial \Psi}{\partial E_{ij}} \dot{E}_{ij}$$ \hspace{1cm} (2.7)

Comparing equations (2.6) and (2.7), we obtain the second Piola-Kirchoff stress tensor $\mathbf{S}$ as,

$$\mathbf{S} = \frac{\partial \Psi}{\partial \mathbf{E}}$$ \hspace{1cm} (2.8)

Rewriting $\mathbf{S}$ in terms of $\mathbf{C}$ instead of $\mathbf{E}$ gives,

$$\mathbf{S} = 2 \frac{\partial \Psi}{\partial \mathbf{C}}$$ \hspace{1cm} (2.9)

The strain energy potential function is typically expressed in the form of $\Psi = \Psi(I_1, I_2, I_3)$, where $I_1, I_2, I_3$ are the first, second and third invariants of the right Cauchy-Green deformation tensor and are defined as,

$$I_1 = \text{tr} \, (\mathbf{C}) = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$ \hspace{1cm} (2.10)

$$I_2 = \frac{1}{2} \left( I_1^2 - \text{tr} \, (\mathbf{C}) \right) = (\lambda_1 \lambda_2)^2 + (\lambda_2 \lambda_3)^2 + (\lambda_3 \lambda_1)^2$$ \hspace{1cm} (2.11)

$$I_3 = \det(\mathbf{C}) = (\lambda_1 \lambda_2 \lambda_3)^2$$ \hspace{1cm} (2.12)

where $\lambda_i$ (i = 1,2,3) are the principal stretch ratios.

Applying the chain rule to equation (2.9), we get,

$$\mathbf{S} = 2 \left( \frac{\partial \Psi}{\partial I_1} \frac{\partial I_1}{\partial \mathbf{C}} + \frac{\partial \Psi}{\partial I_2} \frac{\partial I_2}{\partial \mathbf{C}} + \frac{\partial \Psi}{\partial I_3} \frac{\partial I_3}{\partial \mathbf{C}} \right)$$ \hspace{1cm} (2.13)
It can be shown that the derivatives of strain invariants with respect to $C$ are given as,

$$\frac{\partial l_1}{\partial C} = I$$ (2.14)

$$\frac{\partial l_2}{\partial C} = l_1 I - C$$ (2.15)

$$\frac{\partial l_3}{\partial C} = l_3 C^{-1}$$ (2.16)

Therefore, equation (2.13) becomes,

$$S = 2\left(\frac{\partial \Psi}{\partial l_1} I + \frac{\partial \Psi}{\partial l_2} (l_1 I - C) + \frac{\partial \Psi}{\partial l_3} l_3 C^{-1}\right)$$ (2.17)

The Cauchy stress tensor $\sigma$ is related to the second Piola-Kirchoff stress tensor $S$ through

$$\sigma = \frac{1}{l} F S F^T$$ (2.18)

Since the left Cauchy-Green deformation tensor is defined as $B = F F^T$, we have

$$\sigma = \frac{2}{l} \left(\frac{\partial \Psi}{\partial l_1} B + \frac{\partial \Psi}{\partial l_2} (l_1 B - BB) + \frac{\partial \Psi}{\partial l_3} l_3 I\right)$$ (2.18)

For the incompressible case, $l_3 = 1, \Psi = \Psi(l_1, l_2)$. Therefore equation (2.18) takes the form:

$$\sigma = -p I + 2 \left(\frac{\partial \Psi}{\partial l_1} I + l_1 \frac{\partial \Psi}{\partial l_2}\right) B - 2 \frac{\partial \Psi}{\partial l_2} BB$$ (2.19)

where $p$ is the hydrostatic pressure.

As a phenomenological model, one could assume that the strain energy potential functions $\Psi$ for incompressible materials takes the form of polynomial or reduced polynomial. The general form of a potential function can be written as:

$$\Psi = \sum_{i+j=1}^{N} C_{ij} (l_1 - 3)^i (l_2 - 3)^j$$ (2.20)

where $C_{ij}$ are material constants and $N = 1, 2, 3 \ldots$
For example, the first order polynomial (N=1) will be of the form:

\[ \Psi = c_{10}(I_1 - 3) + c_{01}(I_2 - 3) \]  

(2.21)

This function is also called as the Mooney-Rivlin strain energy potential function[1].

The reduced polynomial forms can be expressed by substituting \( j=0 \) in equation (2.20) as follows:

\[ \Psi = \sum_{i=1}^{N} c_{i0}(I_1 - 3)^i \]  

(2.22)

In the case of \( i=1 \), one would obtain the Neo-Hookean strain energy potential:

\[ \Psi = c_{10}(I_1 - 3) \]  

(2.23)

If we let \( N=2 \), we have

\[ \Psi = c_{10}(I_1 - 3) + c_{20}(I_1 - 3)^2 \]  

(2.24)

The third order reduced polynomial takes the following form (Yeoh strain energy potential function):

\[ \Psi = c_{10}(I_1 - 3) + c_{20}(I_1 - 3)^2 + c_{30}(I_1 - 3)^3 \]  

(2.25)

The material constants found in the above equations are obtained by curve-fitting (nonlinear regression analysis) the equation with the material test data.

In addition to the above invariant based strain energy potential functions, Valanis and Landel [2] proposed a new method in which \( \Psi \) is calculated as the sum of three separate functions of the three independent stretch ratios:

\[ \Psi = \Psi_1(\lambda_1) + \Psi_2(\lambda_2) + \Psi_3(\lambda_3) \]  

(2.26)
Ogden [3] proposed a new form of the Valanis-Landel strain energy function in which the strain energy potential function is expressed as a series of $\lambda_1^{\alpha_i}, \lambda_2^{\alpha_i}$ and $\lambda_3^{\alpha_i}, (i = 1 \text{ to } N)$ where $\alpha_i$ can be any real number.

$$\psi = \sum_{i=1}^{N} \frac{2\mu_i}{\alpha_i^2} \left( \lambda_1^{\alpha_i} + \lambda_2^{\alpha_i} + \lambda_3^{\alpha_i} - 3 \right)$$

(2.27)

where $\lambda_1\lambda_2\lambda_3 = 1$ and $\mu_i, \alpha_i$ are material constants.

Strain-invariant based potential energy functions cannot represent the strain-hardening characteristics typically exhibited by rubbery materials at a large strain level [4]. Arruda and Boyce [5] proposed a new physics based micro-mechanical constitutive model to include such features. Their model represented successfully the response of rubber materials in uniaxial and biaxial tension, uniaxial and plane strain compression and pure shear. The model is based on an eight chain representation of the macromolecular network structure of the rubber and the non-Gaussian behavior of the individual chains in the network. The Arruda-Boyce strain energy potential function has the following form:

$$\psi = \mu \sum_{i=1}^{8} \frac{c_i}{\lambda_{ii}^{3/2}} \left( I_1^{i} - 3 \right)$$

(2.28)

where $I_1$ is first invariant of Cauchy-Green deformation tensor, $\mu$ (shear modulus) and $\lambda_m$ (locking stretch) are material constants and $C_1 = \frac{1}{2}, C_2 = \frac{1}{20}, C_3 = \frac{11}{1050}, C_4 = \frac{19}{7050}$ and $C_5 = \frac{519}{2673750}$.

Details and use of model proposed by Boyce can be found in [6]. It is an improved version of the above model, as basis for developing the new model is explained in Chapter 5.
2.5 Viscoelasticity

Viscoelastic materials have properties which are intermediate between those of an elastic solid and a viscous liquid. In an elastic solid, it is assumed that the displacement response to load is reversible. In case of the viscous liquid, the stress depends on strain rate (based on Newton’s law of viscosity). This viscoelastic phenomenon can be observed in creep and relaxation tests and also in cyclic loading processes [18].

Theory of viscoelasticity can be studied in two categories: linear viscoelasticity and nonlinear viscoelasticity. They can be represented mathematically by history integral or differential forms. More than the history integral forms, the differential constitutive forms are commonly used because of their usage of parameters such as stress/strain and stress/strain rates, instead of relaxation and creep kernels. In addition, the differential forms are phenomenologically based models which can be directly related to spring and dashpot elements [19].

2.5.1 Linear viscoelasticity

Linear viscoelasticity generally describes the polymer behavior in the small strain range. In addition, it has been used to model long-term responses such as creep and stress relaxation. In linear viscoelasticity, springs (elastic elements) and dashpots (viscous elements) form the basic components of a constitutive equation. By altering the number of springs, dashpots and their connections, different material behaviors can be predicted. Two examples of such basic models are Kelvin (or) Voigt model (see Fig 2.3 (a)) and Maxwell model (see Fig 2.3 (b)). The Maxwell model predicts the stress relaxation very well, and the Kelvin (or) Voigt model is good in predicting the creep [20]. As noted previously, polymers exhibit more complex behavior than
either of these two simple models can predict. Hence, generalized models are used to describe such complex behaviors.

Under linear viscoelasticity, Prony-series (many Maxwell elements in parallel with a single spring) are also used to predict the responses of polymer. Use of Prony series can be highly difficult in many cases. This is due to the fact that elements in excess of 20 or more are usually needed to get a better approximation of some real time applications. In addition, the use of generalized Maxwell model (Maxwell elements in parallel) or the generalized Voigt model (Voigt elements in series) is difficult since they involve many material constants that need to be determined through several experiments.

![Diagram of Kelvin or Voigt model and Maxwell model](image)

**Figure 2.3. Linear viscoelastic models: (a) Kelvin or Voigt model, (b) Maxwell model.**

One of the simplest models used to describe a polymer is the ‘standard linear solid’ and is attributed to Zener [21]. It is obtained by adding a spring element in parallel with a Maxwell element (see Fig 2.4). The stress-strain relationship of a standard linear solid model is of the form:

\[
\frac{\eta}{E_1} \frac{d\sigma}{dt} + \sigma = \frac{\eta}{E_1} (E_1 + E_2) \frac{d\varepsilon}{dt} + E_2 \varepsilon
\]  

(2.29)
where $\eta$, $E_1$ and $E_2$ are material constants, and $\sigma$ and $\varepsilon$ are stress and strain respectively. Polymer behavior such as creep, stress-relaxation and rate-dependence can be modeled using this model.

\[ \text{Figure 2.4. Standard linear solid model.} \]

Linear viscoelasticity follows the Boltzmann superposition principle [22]. In most of the cases, linear viscoelasticity fails to predict the observed polymer responses and so nonlinear viscoelasticity is needed.

### 2.5.2 Nonlinear viscoelasticity

In case of Nonlinear viscoelasticity, the stress depends on the entire deformation history; or alternatively, the strain depends on the entire stress history [23]. Bergstrom and Boyce [9] developed a rate-dependent constitutive model for rubber subjected to time-dependent strain histories. But its direct application to HDPE is not well known. Dusunceli and Colak [15] developed a constitutive model for HDPE using viscoplasticity theory based on overstress (VBO). The VBO model is based on test data of HDPE behavior in room temperature which is not suitable to describe behavior of HDPE at high temperatures. In their study, Dusunceli and Colak [15] observed that the elasto-viscoplasticity model proposed by Boyce [6] for polyethylene terephthalate (PET) was not good enough to simulate HDPE.
Shepherd et al. [8] proposed an internal state variable based strain rate and temperature dependent constitutive model to characterize PET. In this model, the major morphological mechanisms in polymers during deformation, including entanglement slippage, orientation, and strain induced crystallization were taken as internal state variables and their evolution under deformation was captured. From the stress-strain results comparison, it is understood that the introduction of evolution based equations into a rubber elasticity model can improve the prediction of polymer behavior very well. But due to the large number of material constants involved in the model, many experiments are needed to identify the parameters. In addition, numerical implementation and simulation was found to be very expensive. Recently, Ayoub et al. [14] proposed a physical-based inelastic model to describe finite strain deformation of HDPE. But again their model was based on test data of HDPE behavior in room temperature.

Based on the review of the existing model, it seems few have concentrated the HDPE at high temperature and high strain rate. Hence a new constitutive model that is specifically targeted at these ranges is required.
Chapter 3

Experiments

This chapter discusses the specimen and the experimental technique used in this study to obtain the material characteristics, i.e., the stress-strain behavior of HDPE under high temperature and high strain. The measured stress-strain responses will be used to calibrate the constitutive model. Monotonic uniaxial compressive tests are performed on compression molded cylindrical specimens at a temperature of 100°C and strain rate of 1/second. The tests are conducted according to ASTM D 695-02a specifications, i.e., standard test method for compressive properties of rigid plastics [24]. Tests are conducted on five specimens in order to confirm the repeatability of the results.

3.1 Test material

The HDPE material used in the testing was Marlex 9503H, which is described as a “gas phase, high molecular weight hexene copolymer with antistatic agent” based on the Chevron Phillips product data sheet [7] and it is tailored for light weight blow molded containers that

- require outstanding Environmental Stress Cracking Resistance (ESCR)
- require excellent impact resistance
- are durable and recyclable for sustainability

Typical blow molded applications for 9503H include detergent bottles, industrial containers and large parts, household and industrial chemical containers.
The nominal physical properties can be found from the product data sheet [7] and are given in table 3.1.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Nominal Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.946 g/cm$^3$</td>
<td>ASTM D1505</td>
</tr>
<tr>
<td>Tensile Strength at Yield (2 in/min, Type IV bar)</td>
<td>24 MPa</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>Britteness Temperature (Type A, Type I specimen)</td>
<td>$&lt;-75^\circ$C</td>
<td>ASTM D746</td>
</tr>
<tr>
<td>ESCR (Condition B -100% Igepal, F50)</td>
<td>$&gt;800$ h</td>
<td>ASTM D1693</td>
</tr>
</tbody>
</table>

Table 3.1. Nominal physical properties of Marlex 9503H.

3.2 Test specimen

The test specimen is prepared in the form of a cylinder with diameter 25.5 mm and thickness of 11.4 mm (Figure 3.1). The specimens are prepared by compression molding technique.

Figure 3.1. Geometry of monotonic uniaxial compressive test specimen.
As mentioned in section 7.1 of ASTM standard D 695-02a [24], the specimen is conditioned in accordance with Procedure A of Practice D 618 at 23 ± 2°C and 50 ± 5% relative humidity for 40 hours prior to the test.

### 3.3 Test method

Based on ASTM standard D 695-02a, section 10 [24], the method of testing is as follows:

1) An INSTRON Universal Testing Machine is used to test the specimens.

2) The test specimen at a temperature of 100°C is placed in between the surfaces of the compression tool, taking care to align its center line with that of the plunger and the ends of the specimen are parallel with the surface of the compression tool. Sufficient lubrication is applied between platens and specimen in order to reduce barreling.

3) The crosshead of the testing machine is adjusted until it just contacts the top of the compression tool plunger. The crosshead speed is set to 684 mm/min which corresponds to a strain rate of one per second.

4) The loads and corresponding compressive strain are noted to get the complete load-deformation curve.

5) Based on the load-deformation curve and original cross sectional area, engineering stress-strain curve is plotted.

6) Modulus of elasticity is calculated by finding the slope of the initial linear portion of the engineering stress-strain curve.
3.4 Test results

The engineering stress vs. engineering strain results of HDPE tested at 100°C under strain rate of one per second for all five specimens are plotted in Fig (3.2).

The true stress and strain are related to the engineering stress and strain as explained below:

\[ \lambda = e + 1 \]  \hspace{1cm} (3.1)
\[ \varepsilon = \ln (\lambda) \]  \hspace{1cm} (3.2)
\[ \sigma = \lambda P \]  \hspace{1cm} (3.3)

where \( \lambda \) is the experimental stretch, \( e \) is the experimental strain, \( P \) is the experimental stress, \( \varepsilon \) is the true strain and \( \sigma \) is the true stress.

Using the above relations, the true stress and true strain values of sample no.5 was calculated and plotted in Fig (3.3) which will be referred from here on to develop and compare the new constitutive model. The experimental strain data of sample no.5 will be used as an input to the developed material model and the stress output will be compared with the experimental true stress vs. true strain plot to validate the model.
Figure 3.2. Uniaxial compression behavior of HDPE at 100°C and strain rate of 1/s.
Figure 3.3. True stress vs. True strain compressive behavior of HDPE Sample 5.
Chapter 4

Comparison of test data with existing models

The finite element preprocessing software ABAQUS/CAE of Dassault Systemes was used for the purpose of evaluating the monotonic uniaxial compressive test data from Chapter 3. Comparison with existing hyperelastic material models are made based on data fitting. ABAQUS has built-in material evaluation capability which was used for the curve fitting. Both linear or non-linear least squares curve fit procedures are employed based on the hyperelastic strain energy potential selected. The relative error norm to be minimized is of the following form

$$ e = \sum_{i=1}^{n} \left( 1 - \frac{\sigma_i^{th}}{\sigma_i^{test}} \right)^2 $$ \hspace{1cm} (4.1)

where $\sigma_i^{test}$ is the stress value from the test data and $\sigma_i^{th}$ is the theoretical stress calculated based on the selected strain energy potential [28].

The existing hyperelastic strain energy potential forms used to fit the test data are as follows:

1) Polynomial (N=1, Mooney-Rivlin model)
2) Polynomial (N=2)
3) Reduced polynomial (N=1, Neo-Hookean model)
4) Reduced polynomial (N=3, Yeoh model)
5) Ogden model
6) Arruda-Boyce model

7) Van der Waals model

4.1 Curve fitting of test data

Two criteria are used for the comparison: visual check and stability. Visual check is done by comparing the plots of material model stress-strain results (which are obtained by the least-square fit) with that of experimental test results. Material is defined to be stable if it satisfies the Drucker postulate, which requires that the change in Kirchhoff stress (Cauchy stress in case of incompressible hyperelastic materials) following from an infinitesimal change in the logarithmic strain must satisfy the inequality,

$$\partial \sigma : \partial \varepsilon > 0 \quad (4.2)$$

In other words, a deformable material is said to be stable if the work done by incremental loads through displacements is positive or zero.

ABAQUS checks the stability in the stretch range $0.1 \leq \lambda \leq 10.0$ (nominal strain range of $-0.9 \leq \varepsilon \leq 9$) for the following deformation modes:

- Uniaxial tension and compression
- Equibiaxial tension and compression
- Planar tension and compression

If instability is found, the preprocessor issues a warning message in the .dat file (data output file) and prints the smallest nominal strains at which the instability occurs in a particular deformation mode.
The monotonic uniaxial compressive test data from Chapter 3 was fit to the various existing hyperelastic material models and the results from ABAQUS were evaluated based on the above two criteria. The fit can be categorized as good or bad, based on how closely the stress results of the material model matches with the stress results from the experiments. Stability limits can be read from the data output files. The comparison of engineering (nominal) stress vs. strain plots and the material stability results are given below in Figs (4.1) to (4.7).

Figure 4.1. Nominal stress-strain plot – Polynomial (N=1) model vs. Test data.
Figure 4.2. Nominal stress-strain plot – Polynomial (N=2) model vs. Test data.

Figure 4.3. Nominal stress-strain plot – Reduced polynomial (N=1) model vs. Test data.
Figure 4.4. Nominal stress-strain plot – Reduced polynomial (N=3) model vs. Test data.

Figure 4.5. Nominal stress-strain plot – Ogden (N=3) model vs. Test data.
Figure 4.6. Nominal stress-strain plot – Arruda-Boyce model vs. Test data.

Figure 4.7. Nominal stress-strain plot – Van der Waals model vs. Test data.
<table>
<thead>
<tr>
<th>Model no</th>
<th>Hyperelastic Material Model</th>
<th>Fit</th>
<th>Stability in Compression mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polynomial (N=1, Mooney Rivlin model)</td>
<td>Bad</td>
<td>Unstable at strains less than -0.4593</td>
</tr>
<tr>
<td>2</td>
<td>Polynomial (N=2)</td>
<td>Good</td>
<td>Unstable at strains less than -0.2818</td>
</tr>
<tr>
<td>3</td>
<td>Reduced polynomial (N=1, Neo-Hookean)</td>
<td>Bad</td>
<td>Stable for all strains</td>
</tr>
<tr>
<td>4</td>
<td>Reduced polynomial (N=3, Yeoh)</td>
<td>Bad</td>
<td>Unstable at strains less than -0.3390</td>
</tr>
<tr>
<td>5</td>
<td>Ogden (N=3)</td>
<td>Good</td>
<td>Unstable at strains less than -0.2938</td>
</tr>
<tr>
<td>6</td>
<td>Arruda-Boyce</td>
<td>Bad</td>
<td>Stable for all strains</td>
</tr>
<tr>
<td>7</td>
<td>Van der Waals</td>
<td>Bad</td>
<td>Unstable at strains less than -0.8292</td>
</tr>
</tbody>
</table>

**Phenomenologically based models**

**Physically based models**

Table 4.1. Evaluation summary of curve fitting of test data.
4.2 Evaluation of curve fitting results

Based on the Figures (4.1) to (4.7), the following conclusions have been made.

Neo-Hookean and Arruda-Boyce models are stable for all strains but large discrepancies are observed in the strain range of interest. Although Van der Waals model is stable in the strain range of interest, it also deviates significantly from the test data. Polynomial (N=2) and Ogden (N=3) gives a good fit, but they are unstable below strain of approximately -0.3 which doesn’t satisfy the strain range of interest.

From the summary, it is clearly understood that none of the existing hyperelastic models, neither the phenomenologically based nor the physics-based models fit the compression test data well. Hence a new material model (i.e. constitutive model) needs to be established to account for the stress-strain relation in the range of interest. This is discussed in the next chapter.
Chapter 5

Constitutive model

5.1 Analysis of HDPE stress-strain behavior

The stress-strain behavior as depicted in Fig (3.3) shows that HDPE exhibits a stiff initial response (with linear elastic modulus), followed by a rollover to flow and then a near constant stress. Based on [14, 15], each of this behavior is found to be dependent on strain rate. Therefore, it is clear that HDPE material exhibits non-linear strain rate dependency. Even at low strains, an increase in the strain rate results in an increase in the stresses. From [6, 20] it is understood that semi-crystalline polymers such as HDPE exhibit high temperature dependence in addition to rate dependence. Hence an attempt is made in this chapter to develop a new constitutive model that incorporates these basic mechanisms.

5.2 Constitutive model development

The constitutive model developed by Boyce [6] to model the finite deformation stress-strain behavior of polyethylene terephthalate (PET) at temperatures above the glass transition temperature is used as a basic framework for the proposed model. It is developed by incorporating network parameters based on molecular dynamics simulations presented in Shepherd [6] model for PET.
The overall deformation of HDPE can be captured as a response to overcome two basic resistances:

1) An intermolecular resistance to deformation;

2) A network resistance to deformation due to molecular orientation;

The intermolecular resistance results in the initially stiff elastic response and the network resistance produces the strain hardening/stiffening behavior resulting from molecular alignment. The strain rate and temperature dependency is due to the time/thermal dependent motion of polymer chains.

The schematic representation of this model behavior is depicted below in Fig (5.1).

![Figure 5.1. Material model: (a) schematics, (b) analog model using spring/dashpot elements.](image-url)
5.2.1 Mathematical model formulation

The mathematical model formulation is based on the analog model Fig (5.1) in which the overall deformation is represented as intermolecular resistance (Resistance A) acting in parallel with a molecular network resistance (Resistance B).

In the proposed model, the deformation gradients associated with the intermolecular ($F_i$) and network resistances ($F_n$), are both equal to the imposed continuum deformation gradient, $F$.

$$F = F_i = F_n \quad (5.1)$$

Using a similar method as given in Ref.[9], each resistance behavior is formulated separately to calculate the stress arising out of that resistance and then finally adding those stresses to derive the total stress.

5.2.2 Resistance A: Intermolecular resistance

In the analog model, Element A, i.e. the spring in series with the viscous element (dashpot) represents the initial elastic response followed by the nonlinear transition to inelastic flow. The deformation gradient $F_i$, can therefore be decomposed into an elastic component, $F_i^e$ and an inelastic component, $F_i^p$ using the multiplicative decomposition [26] as,

$$F_i = F_i^e F_i^p \quad (5.2)$$

The Cauchy stress due to elastic spring and viscous dashpot (Resistance A) can be determined from the elastic Hencky strain as follows:

$$\sigma_i = \frac{1}{j_e} \mathbf{C} : (\ln \mathbf{V}_i^e) \quad (5.3)$$
where $J_e = \det \mathbf{F}_e^e$, $\mathbf{C}$ is the elasticity tensor, and $\mathbf{V}_i^e$ is the left Cauchy green tensor of the elastic deformation gradient which is defined as,

$$
\mathbf{V}_i^e = \left( \mathbf{F}_i^e \mathbf{F}_i^e T \right)^{\frac{1}{2}}
$$

(5.4)

Similar to the Boyce model [6], the flow rule is taken as,

$$
\mathbf{D}_i^p = \dot{\gamma}^p \mathbf{N}
$$

(5.5)

where $\mathbf{D}_i^p$ is the rate of inelastic deformation, $\dot{\gamma}^p$ is the inelastic shear strain rate, and $\mathbf{N}$ is the normalized deviatoric stress given by,

$$
\mathbf{N} = \frac{1}{\sqrt{2}\tau_i} \mathbf{\sigma}_i'
$$

(5.6)

Here $\mathbf{\sigma}_i'$ is the deviatoric part of the Cauchy stress and $\tau_i$ is the equivalent shear stress due to the intermolecular resistance represented as,

$$
\tau_i = \left( \frac{1}{2} \mathbf{\sigma}_i' : \mathbf{\sigma}_i' \right)^{\frac{1}{2}}
$$

(5.7)

To represent the inelastic shear strain rate, $\dot{\gamma}^p$, the double-kink Argon model [12] was used following the Boyce model [6], i.e.,

$$
\dot{\gamma}^p = \dot{\gamma}_0^p \exp \left[ -\frac{A}{kT} \left( 1 - \frac{\tau_i}{s} \right) \right]
$$

(5.8)

where $\dot{\gamma}_0^p$ is reference shear strain rate, $A$ is the energy barrier to flow, and $s$ is the shear resistance taken to be 0.115G, $G$ is the elastic shear modulus, $k$ is the Boltzmann constant and $T$ is the temperature.

The rate kinematics begin with the velocity gradient of intermolecular resistance, given by,
\[ L_i = \dot{F}_i F_i^{-1} \]  
\[ L_i = \dot{F}_i^e F_i^{e-1} + \dot{F}_i^p F_i^{p-1} F_i^{e-1} = L_i^e + L_i^p \]  
\[ L_i^p = D_i^p + W_i^p \]

where \( L_i^p \) is the inelastic velocity gradient which is separated into a symmetric part, \( D_i^p \) representing the inelastic rate of deformation and an anti-symmetric part, \( W_i^p \) that represents the inelastic spin tensor.

The unloaded configuration can be made distinct through several methods [10]; one simple method is to take the spin \( W_i^p = 0 \). This method generally results in elastic and plastic deformation gradients which include rotations. The rate dependent \( F_i^p \) is used as internal state variable (ISV) and solved over time by using \( \dot{F}_i^p \).

### 5.2.3 Resistance B: Network resistance

In Element B, the nonlinear spring represents the resistance to molecular network. The stress due to this network resistance is determined by the network orientation, which is derived from the Arruda–Boyce model [5]. Modifications has been made to the chain density and number of statistical segments between entanglements in the Arruda-Boyce model [5] to incorporate the evolution of entanglements (which accounts for the crystallization) as proposed in the Shepherd model [8].
Based on Shepherd model [8], two opposing mechanisms are proposed for the evolution of the entanglement. One is from the stretch that is imposed on the polymer network. This leads to the tightening of knot-like structures, which poses as additional mechanical constraints for the further development of the entanglements. On the other hand, relative chain slippage and unraveling could take place due to relaxation. This further reduces the number of interconnects and results in entanglement loss. These two basic mechanisms are incorporated in the Shepherd model.

In representing the first mechanism, the number density of rate independent entanglements, $n_{\text{e,base}}$, is taken to be a function directly related to the overall stretch, i.e.,

$$n_{\text{e,base}} = n_{\text{e,init}} \exp[\Delta F_l(\bar{\lambda} - 1)]$$

(5.12)

where $n_{\text{e,init}}$ is the initial number density of entanglements in the undeformed material, $\Delta F_l$ is a scaling parameter that determines the sensitivity of the entanglement density to the overall stretch, and $\bar{\lambda}$ is average principal stretch on each chain of the network.
The rate dependent decrease in the number density of entanglements is taken to depend on the effective shear stress, time, and temperature. The rate of entanglement slippage is calculated from a relation similar to the Arrhenius relationship, i.e.

\[
\dot{n}_{e_{\text{slip}}} = -\dot{n}_{e_0} \exp \left(\frac{-\Delta F_e}{kT}\right) \frac{n_e}{n_{\text{base}}} \tau^{\Delta F_t}
\]  

(5.13)

where \(\dot{n}_{e_0}\) is an entanglement slippage pre-exponential constant, \(\Delta F_e\) is the thermal activation energy, \(\Delta F_t\) is the shear stress activation energy, \(\tau\) is the equivalent total shear stress given by

\[
\tau = \sqrt{\frac{1}{2}} \boldsymbol{\sigma} : \boldsymbol{\sigma}'
\]

where \(\boldsymbol{\sigma}'\) is the deviatoric part of total stress tensor and \(n_e\) is the current number density of entanglements given by,

\[
n_e = n_{\text{base}} \exp \left(\frac{n_{e_{\text{slip}}}}{n_{\text{base}}}\right)
\]  

(5.14)

The above relationship (5.14) based on the Avrami Equation, prevents the number density of entanglements from falling below the baseline number density of entanglements.

The rate dependent \(n_{e_{\text{slip}}}\) is used as internal state variable (ISV) and solved as a function of time by based on \(\dot{n}_{e_{\text{slip}}}\). Considering four chains to terminate at each interconnect, the chain density \(n\), is defined as,

\[
n = 2n_e
\]  

(5.15)

Before calculating the stress due to network resistance, the number of segments [Refer Fig. (5.2)] between interconnects, \(N\), must be updated based on Eqn. (5.16),

\[
N = \frac{N_{as}}{n} = \frac{N_{as}}{2n_e}
\]  

(5.16)
in which it is related to the number density of amorphous statistical segments, \( N_{as} \), and chain density, \( n \).

The resulting network stress can be obtained based on the Arruda-Boyce model [5] and Shepherd model [8],

\[
\sigma_n = \frac{2n_ekT}{3} \ell^{-1} \left( \frac{\lambda}{\sqrt{N}} \right) \left[ B - \frac{\lambda^2}{\lambda} I \right]
\]  

(5.17)

where \( \ell^{-1} \) is the inverse Langevin function. The Langevin function is given by \( \ell(x) = \coth(x) - (1/x) \). Total stress tensor is given by,

\[
\sigma = \sigma_i + \sigma_n
\]  

(5.18)

Up to this point, the constitutive model is fully described. For the HDPE under study, material constants (\( E, \nu, A, \gamma_0^p, N_{as}, N, \Delta Fe, \Delta Fl, \Delta Ft, \hat{n}_e \)) involved in the constitutive model are listed in Table (5.1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus, ( E )</td>
<td>235 MPa</td>
<td>Fit</td>
<td>(5.3)</td>
</tr>
<tr>
<td>Poisson ratio, ( \nu )</td>
<td>0.47</td>
<td>Fit</td>
<td>(5.3)</td>
</tr>
<tr>
<td>Energy barrier to flow, ( A )</td>
<td>( 2 \times 10^{-20} )</td>
<td>[14]</td>
<td>(5.8)</td>
</tr>
<tr>
<td>Reference shear rate, ( \gamma_0^p )</td>
<td>( 1 \times 10^{-6} )</td>
<td>[14]</td>
<td>(5.8)</td>
</tr>
<tr>
<td>Scaling factor, ( \Delta Fl )</td>
<td>1.97</td>
<td>Fit</td>
<td>(5.12)</td>
</tr>
<tr>
<td>Thermal activation energy, ( \Delta Fe )</td>
<td>( 2 \times 10^{-19} )</td>
<td>Fit</td>
<td>(5.13)</td>
</tr>
<tr>
<td>Shear stress activation energy, ( \Delta Ft )</td>
<td>0.01</td>
<td>Fit</td>
<td>(5.13)</td>
</tr>
<tr>
<td>Reference rate of entanglement slippage, $n_{\text{e}_0}$</td>
<td>$9.19 \times 10^{31}$</td>
<td>Fit</td>
<td>(5.13)</td>
</tr>
<tr>
<td>Entanglement density, $N$</td>
<td>100</td>
<td>[14]</td>
<td>(5.16, 17)</td>
</tr>
<tr>
<td>Amorphous state entanglement density, $N_{\text{as}}$</td>
<td>$8.05 \times 10^{17}$</td>
<td>Fit</td>
<td>(5.16)</td>
</tr>
</tbody>
</table>

Table 5.1. Material constants in the constitutive model.

### 5.3 Schematics of model implementation in FORTRAN

The implementation of proposed material model as a standalone FORTRAN code has two main parts: a wrapper code and material model subroutine. The wrapper code reads in and stores the input stretch and time increment. Once all the necessary initialization or reading in data from stored field variables (stress, strain, deformation gradient, etc., from previous time step) is done, the material model subroutine is called inside the wrapper code for each time increment (loop over total number of time increments). The subroutine does all the calculations involved in the material model and finally gives the stress output and exits the loop. Then the loop continues for next time increment and repeats the process till stress increments for all the time increments are calculated and stored. The schematics of material model implementation are explained below.

**Step 1: Read inputs in the wrapper code**

From input text files, read in experimental time increment (dt) and stretch ($\lambda$)

Calculate current deformation gradient at end of time step

$$ F_1 = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{\lambda}} \end{bmatrix} $$

**Step 2: Material model subroutine**

Initializing:
1) $n_{\text{e}_\text{slip}} = 0$
2) \( F^p_i = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \)

**Step 3: Solving for derivatives of \( n_{e\_slip} \) and \( F^p_i \)**

Solving for derivatives using Forward Euler method with time step, \( dt \)

- Interpolate and find \( F \), using \( F_0, F_1 \) and \( dt \)
- Find \( B = F F^T \) (left Cauchy green tensor)
- Find eigenvalues and eigenvector of \( B \)

**Step 4: Calculate derivative of \( F^p_i \)**

- \( F^p_i = F F^p_i^{-1} \) (we know \( F = F_i \))
- \( J_e = \det F^p_i \)
- \( V^e_i = \left( F_i^e F_i^{eT} \right)^{1/2} \)
- Find eigenvalues and eigenvector of \( V^e_i \)
- Find principal true strain and true strain tensor, \( \varepsilon_i \)
- Intermolecular stress, \( \sigma_i = \frac{1}{J_e} C : (\ln V^e_i) \)
- \( \tau_i = \left( \frac{1}{2} \sigma_i : \sigma_i \right)^{1/2} \)
- \( \dot{\gamma}^p = \dot{\gamma}_0 \exp \left[ -\frac{A}{kT} \left( 1 - \frac{\tau_i}{\frac{s}{2}} \right) \right] \)
- \( D^p_i = \dot{\gamma}^p \frac{1}{\sqrt{2s_i}} \sigma_i' \)
- From kinematics, \( D^p_i = F^e_i \dot{F}^p_i F_i^{p^{-1}} F_i^{e^{-1}} \)
  So, \( \ddot{F}^p_i = F_i^{e^{-1}} D^p_i F_i^{e} F^p_i \)

**Exit: Step 4**

- Calculate \( n_{e\_base} \)
- Calculate \( n_{e} \)
- Calculate \( N = \frac{N_{as}}{n} = \frac{N_{as}}{2n_{e}} \) (\( n_{e\_initial} \) is found using this equation and initial \( N \) as input)
- Network stress vector, \( \sigma_n = \frac{2n_{as} kT \sqrt{N}}{3} \ell^{-1} \left( \frac{\lambda}{\sqrt{N}} \right) \left[ B - \lambda^2 I \right] \)
- Rotate by eigenvector to get stress tensor \( \sigma_n \)
- Find \( \sigma = \sigma_i + \sigma_n \)
- \( \tau = \left( \frac{1}{2} \sigma' : \sigma' \right)^{\frac{1}{2}} \)

**Step 5: Calculate derivative of \( n_{e \text{ slip}} \)**

- \( \dot{n}_{e \text{slip}} = -n_{e_0} \exp \left( \frac{-\Delta F_e}{kT} \right) \frac{n_e}{n_{\text{base}}} \tau \Delta t \)

**Exit: Step 5**

Store, derivatives of \( n_{e \text{ slip}} \) and of \( F^p_1 \)

Update \( n_{e \text{ slip}} \) and \( F^p_1 \) by Forward Euler method

**Exit: Step 3**

Store updated \( n_{e \text{ slip}} \) and \( F^p_1 \) as internal state variables (ISV’s) to use in next time increment

**Exit: Step 2**

Store the current \( \sigma \), and \( F_1 \) as \( F_0 \), in field variables to be used in next time increment

**Exit: Step 1**
Chapter 6

Results and discussion

In this chapter, the true stress-strain results obtained from the proposed material model are compared with the monotonic uniaxial compressive test results. In addition, several other forms of inelastic flow rules are implemented and stress results due to these changes are compared. The sensitivity of stress results to the change in parameters, $\dot{\gamma}_0$ (reference shear strain rate) and $A$, (energy barrier to flow) is studied. Finally, an investigation on the influence of the stress due to network resistance to deformation in the material model is presented.

6.1 Comparison of material model and experimental results

The comparison between experimental true stress and output from the proposed material model based on input experimental true strain is depicted below in the Fig (6.1). Although most part of the elastic and plastic region matches very closely with the experimental results, the transition from elastic to plastic region is not well captured. The material model overestimates the stresses with a steep rise and then flow into plastic region. This calls for further improvement in the flow rule used in the model.
6.2 Comparison of different material model flow rules

In order to improve the accuracy of the model, different forms of inelastic flow rule are studied and implemented in the proposed model. These forms are explained in brief and the material model stress results using these flow rules are compared with experimental stress results and with one another as well.
6.2.1 Bergstorm-Hybrid model

In the Ref. [27], Bergstrom et al. has proposed a new hybrid model in which power-law form of plastic flow rate has been used.

The inelastic shear strain rate, $\dot{\gamma}^p$ is represented as,

$$\dot{\gamma}^p = \left(\frac{\tau}{\tau_{\text{base}}}\right)^m(\varepsilon_p)$$

(6.1)

where the exponent $m(\varepsilon_p)$ evolves as a function of plastic strain as described below:

$$m(\varepsilon_p) = \begin{cases} m_f + (m_i - m_f) \left[1 - \frac{\varepsilon_p}{\tilde{\varepsilon}_2}\right]^\alpha, & \text{if } \varepsilon_p < \tilde{\varepsilon}_2 \\ m_f, & \text{otherwise} \end{cases}$$

(6.2)

and $m_i, m_f, \tilde{\varepsilon}_2, \alpha$ are material constants and $\varepsilon_p$ is the effective plastic strain defined as,

$$\varepsilon_p = \sqrt[\frac{2}{3}]{(\varepsilon_p; E_p)^\frac{1}{2}}$$

(6.3)

where $E_p$ is the true plastic strain tensor (logarithmic plastic strain tensor).

The material constants involved in these equations are obtained through fitting. The specific values are $m_i = 3.91$, $m_f = 3.908$, $\tilde{\varepsilon}_2 = 1.179$, $\alpha = 0.499$ and $\tau_{\text{base}} = 94$. Figure (6.2) shows the comparison of this model prediction and the experiment results.

6.2.2 Bergstorm-Boyce model

Based on the Bergstrom-Boyce model [9], a simplified version of power law type plastic flow rate equation is used in this study. The inelastic shear strain rate, $\dot{\gamma}^p$ is represented as,

$$\dot{\gamma}^p = \left(\frac{\tau}{\tau_{\text{base}}}\right)^m$$

(6.4)
where $\tau_{\text{base}}$ and $m$ are material constants. Figure (6.2) shows the comparison of the model predictions based on $\tau_{\text{base}} = 300$ and $m = 2.3$ with the experiment.

### 6.2.3 Ayoub model

In the model proposed by Ayoub et al. [14], the inelastic shear strain rate, $\dot{\gamma}^p$ is represented as,

$$\dot{\gamma}^p = \frac{3}{2} \left( \sqrt{3} \frac{\tau}{D} \right)^m$$  \hspace{1cm} (6.5)

where $D$ and $m$ are material constants. A comparison between the modeling prediction using $D = 40$ and $m = 32$ with the experiment is shown in Fig (6.2).

![Comparison plot of True Stress vs. True Strain](image)

**Figure 6.2.** Comparison of true stress vs. true strain results of experimental and constitutive model with all flow rules.
6.2.4 Discussion on the Comparison

On studying the stress results of all different flow rules from Fig (6.2), it can be seen that these flow rules also lead to perfect match in elastic region, close match in plastic region (except Bergstrom-Boyce model) but the flow pattern from elastic to plastic region still needs improvement.

This difference can be attributed to the reason that all these models are used to predict the stress-strain behavior of either different material (like PET) or at room temperature or under low strain rate conditions.

6.3 Parametric study of inelastic flow rate in proposed model

In the proposed model, the sensitivity of stress results to the change in parameters, \( \dot{\gamma}_0^p \) (reference shear strain rate) and A, (energy barrier to flow) in the inelastic shear strain rate equation (5.8) is studied. More specifically, the parameter A is changed from \( 2 \times 10^{-20} \) to \( 2.5 \times 10^{-20} \) J, and the reference shear strain rate is changed from \( 1 \times 10^{-6} \) to \( 0.8 \times 10^{-6} \) s\(^{-1} \). The results are shown in Fig (6.3). It is seen that an increase in A will generally result in reduction of yield stress. In contrast, any decrease in the reference shear rate will result in increase in the yield stress. The shape of the stress-strain curve is relatively insensitive to the change in these two parameters.
Figure 6.3. Parametric study of true stress vs. true strain results of constitutive model with the proposed model flow rule.

From the model development explained in Chapter 5, we know that the total stress is calculated as the sum of stresses due to two individual resistances (intermolecular and network). i.e.

\[ \sigma = \sigma_i + \sigma_n \]  \hspace{1cm} (6.6)

The influence of these resistances in the material model is studied by equating the total stress to intermolecular stress and network stress separately. i.e.

\[ \sigma = \sigma_i \] \hspace{1cm} (6.7)

\[ \sigma = \sigma_n \] \hspace{1cm} (6.8)
Figure 6.4. Influence of stress due to network resistance on material deformation.

From the Fig (6.4) it can be seen that there is very little influence of stress due to the network resistance (In material model schematics represented by Resistance B: Network resistance to deformation due to molecular orientation).

It should be noted that the network resistance is responsible for the strain hardening/stiffening behavior of polymer resulting from the molecular alignment. Since in our experimental case of 100°C and strain rate of 1/s on HDPE, the hardening behavior is not pronounced and it can be concluded that the network portion of the model may not be significant. Another possible reason could be due to the lack of hardening behavior in this
particular strain range of interest and the employed strain rate condition. Since the two mechanisms produce very similar effects, the material model is incorporated with the stress due to network resistance to deformation.

To summarize, the proposed material model can capture the uniaxial compressive stress-strain behavior of HDPE under high strain rate and high temperature. The prediction provides good agreement in both the elastic and plastic regions. There are discrepancies in fitting the transition region with the existing flow rules.
Chapter 7

Summary and Future scope of work

In this thesis, a constitutive model to predict the stress-strain behavior of high density polyethylene under high strain rate and high temperature is presented. Its effectiveness and accuracy is evaluated by comparison with the experimental results. Based on the progress made up to date, the following scope can be incorporated into this work in the future.

1) More work can be done to improve the flow rule in order to predict more realistic flow pattern from elastic to plastic region. More specifically
   - Evolution parameters can be introduced into the flow rule equation;
   - Amorphous and crystalline phases can be individually modeled by introducing additional spring with dashpot in parallel into the existing intermolecular resistance;

2) More physical experiments can be carried out to capture the creep, relaxation and unloading behavior of HDPE under different temperatures and strain rates. If necessary, new parameters shall be incorporated in the material model to predict these behaviors.
   - Due to its strain rate and temperature dependency, and being subjected to variable operating conditions during manufacturing, the material model needs to be fitted to test data at different temperatures, strain rates (loading and unloading) which will further improve the use of model for several applications;
- Polymers exhibit the viscous effects, creep and relaxation, due to delayed response of the underlying polymer network chains. Hence in order to incorporate their impact in the end product’s design parameters, the material model needs to be validated with these characteristics as well;

3) The material model can be implemented as a user subroutine into commercial finite element software (e.g. ABAQUS).

- Model can be implemented as user subroutine (Implicit or Explicit formulation) in ABAQUS for a test case (e.g. uniaxial compression) on a single three dimensional element with appropriate boundary and loading conditions and the results can be compared with the experimental results;

4) The user subroutine can be applied in finite element analysis of polymer products or polymer manufacturing processes which uses HDPE.

- The user subroutine can be implemented in the FE analysis of manufacturing process such as thermoforming or products such as pipes and the behavior of polymer under loading conditions can be compared with actual results from product testing; (e.g. maximum displacement, maximum stress, etc.)
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