A Constitutive Model for Predicting the Large Deformation Thermomechanical Behavior of Fluoropolymers

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Abstract

This paper presents a newly developed constitutive model for predicting the time- and temperature-dependent mechanical behavior of fluoropolymers, including PTFE, PFA and FEP. The mathematical details of the theory and its connection with the underlying microstructure are presented together with aspects of its numerical implementation into large-strain finite element simulations. A set of uniaxial tension, uniaxial compression, hydrostatic compression, multi-cycle thermomechanical, and small sample punch (disk bend) tests were performed on glass fiber filled PTFE to evaluate the predictive capabilities of the model. The tests were performed using monotonic and cyclic load histories, at different deformation rates and temperatures. A direct comparison between the experimental data and the model predictions show that the constitutive theory accurately captures the material response. The model is also capable of predicting the influence of hydrostatic stress on both the deviatoric and volumetric flow rates, enabling accurate predictions of fluoropolymers with small amounts of porosity.

1 Introduction

Fluoropolymers are a class of polymers defined by the presence of carbon (C) and fluorine (F), that have many unique mechanical and chemical properties. For example, fluoropolymers have a lower friction coefficient than almost any other solid material, and the chemical resistance and thermomechanical stability of fluoropolymers are better than most other polymeric materials. The era of fluoropolymers started in 1938 when R. Plucket of DuPont invented polytetrafluoroethylene (PTFE) (Ebnesajjad, 2000). This material, which is based on the monomer \([(-CF_2-CF_2)^n]\), is the fluoropolymer with the highest chemical inertness and broadest range of temperature use, but due to its very high melt viscosity it is not melt-processable, and therefore difficult to use in some manufacturing applications. A number of chemical modifications to PTFE have been introduced to enable more common manufacturing techniques, and hence improve the usability of PTFE.
Some of the more common fluoropolymers, in addition to PTFE are: fluorinated ethylene propylene (FEP), a branched polymer that can be extruded; perfluoroalkoxy resin (PFA), a melt-processable, corrosion and heat resistant resin; and ethylene-tetrafluorethylene copolymer (ETFE), containing hydrogen to increase the mechanical strength at the cost of reducing the thermal and chemical resistance.

In many applications, the use of a fluoropolymer is the only reasonable option, due to operational requirements or environmental conditions. For example, fluoropolymers have found many applications in gaskets and liners for vessels and pipes in applications where chemical resistance is of importance, in high pressure seals for the automotive industry and petrochemical industries, in coatings in various cookware applications, in medical applications, and in architectural fabrics for stadiums and airport roofs. Due to its high cost compared to other polymers, the use of fluoropolymers is always motivated by one or more of its specific properties, which sets it apart from most materials, specifically other polymers.

It is known that unmelted PTFE can have a degree of crystallinity that is higher than 90%, and that the degree of crystallinity of FEP is typically half that of PTFE (Ebnesajjad, 2000). For temperatures above 19°C, the crystal structure of PTFE is hexagonal, and individual molecules are arranged in helical conformations (Blanchet, 1997). These features of the microstructure, together with the broad range of usable temperature, makes the characteristic material response of fluoropolymers particularly challenging to model. The current understanding of how to predict the thermomechanical response of fluoropolymers under thermomechanical loads are for these reasons far from complete. Only recently have more advanced constitutive models for fluoropolymer material models been developed (Khan and Zhang, 2001; Kletschkowski et al., 2002). These models have enabled finite element predictions of the large strain behavior of fluoropolymers, albeit only at isothermal conditions. Furthermore, the accuracy of these models for predicting the behavior in general deformation states has not been reported. The goal of this work was to develop a new accurate model that can be used to predict the behavior of fluoropolymers subjected to multiaxial large-deformation thermomechanical loadings. The theory and predictive capabilities of the new constitutive model are presented in the following sections.

2 Constitutive Modeling of Fluoropolymers

Fluoropolymers, as well as other thermoplastics, exhibit a complicated non-linear response when subjected to external loads. At small deformations, the material response is linear viscoelastic. At larger strains, the
material undergoes distributed yielding, unrecoverable deformation, viscoplastic flow, and finally, gradual material stiffening at large deformations until ultimate failure occurs. It is also known that the material response is strongly dependent on strain-rate and temperature: higher deformation rates and lower temperatures increase the stiffness of the material. In this work we have developed a new model for predicting these experimentally observed characteristics. The proposed model is an extension of previous work by Bergström and Boyce (1998, 2000, 2001) and Arruda and Boyce (1995) for elastomers and glassy polymers.

There are a number of different candidate material models that are documented in the literature for predicting the behavior of general thermoplastics (e.g. Arruda and Boyce (1995); Bergström et al. (2003); Ho and Krempel (2002); Lion (1997)). Development of advanced constitutive models for polymers is an active area of research that is continuously evolving and improving. Up until the last few years, there were no constitutive models specifically developed for fluoropolymers, and the most useful models were either classical isotropic plasticity, linear viscoelasticity models, or general models for thermoplastics (Arruda and Boyce, 1995; Bergström and Boyce, 2000). In the last few years, however, constitutive models specifically developed for fluoropolymers have emerged (Khan and Zhang, 2001; Kletschkowski et al., 2002). These models are typically better at predicting the experimentally observed characteristics of fluoropolymers than traditional isotropic plasticity or viscoelasticity models, but have limitations of isothermal conditions only. In this work we have developed a new framework for predicting the thermomechanical behavior of fluoropolymers. In the following, this new constitutive model is referred to as the Dual Network Fluoropolymer (DNF) model.

The DNF model incorporates experimental characteristics by using a decomposition of the material behavior into a viscoplastic response, corresponding to irreversible molecular chain sliding (due to the lack of chemical crosslinks in the material) and a time-dependent viscoelastic response. The viscoelastic response is further decomposed into the response of two molecular networks acting in parallel: a first network (A) captures the equilibrium (long term) of the viscoelastic response and a second network (B) the time-dependent (short term) deviation from the viscoelastic equilibrium state. A one-dimensional rheological representation of this constitutive framework and a schematic illustrating the kinematics of deformation are shown in Figure 1. The deformation gradient \( \mathbf{F} \) is multiplicatively decomposed into viscoplastic and viscoelastic components: \( \mathbf{F} = \mathbf{F}^{ve} \mathbf{F}^{p} \). The Cauchy stress acting on network A is given by the eight-chain representation (Bergström and Boyce, 2000; Arruda and Boyce, 1993):

\[
\mathbf{T}^{ve} = \mathbf{f}_{sch}(\mathbf{F}^{ve}) = \frac{\mu_{A}(\theta)}{J^{ve} \lambda_{lock}^{ve}} \left( \frac{\lambda^{ve}}{\lambda^{lock}} \right) \text{dev} [\mathbf{B}^{ve}] + \frac{\kappa_{0} \ln[J^{ve}]}{J^{ve}} \mathbf{1},
\]

(1)
Figure 1: (a) Rheological representation of the constitutive model; (b) Kinematics of deformation.

where \( J^{ve} = \det[F^{ve}] \), \( \mu_A(\theta) \) is a temperature dependent initial shear modulus, \( \lambda^{lock} \) is the chain locking stretch, \( B^{ve*} = (J^{ve})^{-2/3} F^{ve} (F^{ve})^T \) is a Cauchy-Green deformation tensor, \( \lambda^{ve*} = (\text{tr} |B^{ve*}|) / 3 \) is the effective chain stretch based on the eight-chain topology assumption (Arruda and Boyce, 1993), \( \mathcal{L}^{-1}(x) \) is the inverse Langevin function, where \( \mathcal{L}(x) = \coth(x) - 1/x \), and \( \kappa_0 \) is the bulk modulus. By explicitly incorporating the temperature dependence of the shear modulus it is possible to capture the stiffness variation of the material over a wide range of temperatures. The following expression is found to accurately capture the experimentally observed temperature dependence of the shear modulus for temperatures between 20°C and 200°C:

\[
\mu_A(\theta) = \mu_A^0 \exp \left[ \frac{\theta_0 - \theta}{\theta_{\text{base}}} \right],
\]  

(2)

where \( \theta_0 = 20^\circ\text{C} \) is a reference temperature, \( \theta \) is the current temperature, and \( \mu_A^0 \) and \( \theta_{\text{base}} \) are specified material parameters.

The viscoelastic deformation gradient acting on network \( B \) is decomposed into elastic and viscous parts: \( F^{ve} = F^e F^v \). The Cauchy stress acting on network \( B \) is obtained from the same eight-chain network representation that was used for network \( A \). For simplicity, the response of network \( B \) is taken as a scalar factor \( s_B \) (a specified material parameter) times the eight-chain expression that was used for network \( A \).
applied on the deformation gradient $F^e$:

$$T^e = s_B \cdot f_{sch}(F^e),$$

(3)

where $f_{sch}(\cdot)$ is the tensorial function defined in Equation (1). Using this framework, the total Cauchy stress in the system is given by $T = T^{ve} + T^e$. The total velocity gradient of network $B$, $L^{ve} = \dot{F}^{ve}(F^{ve})^{-1}$, can similarly be decomposed into elastic and viscous components: $L^{ve} = L^e + F^e L^e F^e^{-1} = L^e \dot{L}^e$, where $L^e = \dot{F}^e F^e^{-1} = D^v + W^v$ and $\dot{L}^e = D^v + \dot{W}^v$. The unloading process relating the deformed state with the intermediate state is not uniquely defined, since an arbitrary rigid body rotation of the intermediate state still leaves the state stress free. The intermediate state can be made unique in different ways (Boyce et al., 1989), one particularly convenient way that is used here is to prescribe $\dot{W}^v = 0$. This will, in general, result in elastic and inelastic deformation gradients both containing rotations. The rate of viscoplastic flow of network $B$ is constitutively prescribed by $\dot{\gamma}^v = \dot{\gamma}^v_{dev} N^v_{dev} + \dot{\gamma}^v_{vol} N^v_{vol}$, where the first term gives the deviatoric viscoelastic flow and the second term gives the volumetric viscoelastic flow. The tensors $N^v_{dev}$ and $N^v_{vol}$ specify the directions of the driving deviatoric and volumetric stresses of the relaxed configuration convected to the current configuration, and the terms $\dot{\gamma}^v_{dev}$ and $\dot{\gamma}^v_{vol}$ specify the effective deviatoric and volumetric flow rates. Noting that $T^e$ is computed in the loaded configuration, the driving deviatoric stress on the relaxed configuration convected to the current configuration is given by $T^e' = \text{dev}[T^e]$, and by defining an effective stress by the Frobenius norm $\tau^e = ||T^e'||_F = (\text{tr}[T^e'T^e'])^{1/2}$, the direction of the driving deviatoric stress becomes $N^v_{dev} = T^e'/\tau^e$. The effective deviatoric flow rate is given by the reptation-inspired equation (Bergström and Boyce, 2000):

$$\dot{\gamma}^v_{dev} = \dot{\gamma}_0 \left[ \frac{\sigma^v}{\tau^e_{base}} + \beta \rho^e \right]^m \left( \frac{\theta}{\theta_{base}} \right)^n,$$

(4)

where $\sigma^v = \sqrt{\text{tr}[B^v^e]}/3$ is an effective viscoelastic chain stretch,

$$B^v^e = (J^v)^{-2/3}F^e(F^e)^T$$

is a Cauchy-Green deformation tension, $\rho^e = -(T^e_{11} + T^e_{22} + T^e_{33})/3$ is the hydrostatic pressure, $\dot{\gamma}_0$ is a constant taken as 1/s (1 reciprocal second) that is needed for dimensional consistency, and $C$, $\beta$, $m$, $\tau^e_{base}$, $n$, and $\theta_{base}$ are specified material parameters. In this framework, the temperature dependence of the flow rate is taken to follow a power law form. Due to the high bulk modulus of PTFE the effective volumetric flow rate is small and is here simply represented with a constant viscosity...
\( \eta_{\text{vol}} : \dot{\gamma}^{v}_{\text{vol}} = \frac{p^e}{\eta_{\text{vol}}} \). In summary, the velocity gradient of the viscoelastic flow can be written

\[
L^v = F^{e-1} \left( \dot{\gamma}^{v}_{\text{dev}} \frac{\text{dev}[T^e]}{\tau^e} + \dot{\gamma}^{v}_{\text{vol}} I \right) F^e. \tag{5}
\]

The rate of plastic flow is captured by a simple phenomenological representation:

\[
\dot{\gamma}^p = \begin{cases} 
abla (\epsilon - \epsilon_0)^{b-1} \dot{\epsilon} & \text{if } \tau > \sigma_0 \\
0 & \text{otherwise}
\end{cases} \tag{6}
\]

where \( a > 0, b > 0 \) and \( \sigma_0 > 0 \) are specified material parameters, \( \tau = ||\text{dev}[T]||_F \) is the Frobenius norm of the deviatoric portion of the Cauchy stress \( T \), and \( \epsilon_0 \) is the effective strain at which \( \tau \) becomes equal to \( \sigma_0 \). The effective strain in Equation (6) is obtained from \( \epsilon = ||E_{ln}||_F \), where \( E_{ln} = \ln[V] \) is the logarithmic strain, and \( \dot{\epsilon} \) is the rate of change of the effective strain. The key feature of Equation (6) is that it predicts the rate of plastic flow to be proportional to the applied strain rate and the magnitude of the current strain. By inserting \( F = F^{ve} F^p \) into \( L = \dot{F} F^{-1} \), the expression for the velocity gradient can be expanded to \( L = L^{ve} + F^{ve} L^p F^{ve} = L^{ve} \dot{L}^p \). By taking \( \dot{W}^p = 0 \), the viscoplastic velocity gradient can be written \( \dot{L}^p = \dot{\gamma}^p \text{dev}[T] / \tau \) giving

\[
L^p = \dot{\gamma}^p F^{ve-1} \frac{\text{dev}[T]}{\tau} F^{ve}, \tag{7}
\]

specifying the rate kinematics of the plastic flow.

### 3 Materials and Methods

Section 3.1 first examines the PTFE material that was studied in this work and the experimental techniques that were used to characterize the material behavior. The methods and procedures that were used to calibrate and validate the predictions from the new Dual Network Fluoropolymer (DNF) model are then described in Section 3.3.

#### 3.1 Experimental

Some of the experimental data presented below were from tests on 15 vol% fiberglass-filled PTFE stock used to fabricate ring seals for use in threaded connections in high-pressure gas wells. The seal rings are
manufactured by a compression molding and sintering process from a granular pelletized PTFE powder, entrained with milled E-type glass fibers. Other test data or experimental results were taken from published experimental data from the sources are indicated.

3.1.1 Uniaxial Tension Tests

In the uniaxial tension experiments, cuboid-shaped specimens with a width of 10 mm, a thickness of 2 mm, and height of 100 mm were loaded in displacement control using an electromechanical load frame. An extensometer mounted at the center of the specimens was used to measure displacements, and a 10 kN load cell was used to measure the applied force. The tests were performed at room temperature (20°C) at different engineering strain rates ranging from 2.0 × 10⁻⁴/s to 2.0 × 10⁻³/s. True stress and true strain were computed from the force and deformation data assuming a homogeneous, incompressible deformation field. A select few stress relaxation tests were also performed. In these experiments the test specimens were deformed at a high deformation rate (\(\dot{\epsilon} = 0.5/s\)) to a strain of 0.01, and then held at that strain for 25 minutes during which the stress relaxation was measured.

3.1.2 Uniaxial Compression Tests

The uniaxial compression experiments were performed on cuboid-shaped specimens with a width of 12 mm, a depth of 12 mm, and a height of 14 mm. The experiments were performed on the same testing machine that was used for the tension tests. In the tests, the applied deformation was obtained from the crosshead displacement. The compression tests were performed at room temperature at an engineering strain rate of -0.005/s. Due to the low friction between the PTFE samples and the loading platens it was not necessary to introduce additional lubrication to avoid an inhomogeneous deformation state. The true stress and strain quantities were obtained from the measured force and displacement data by assuming a homogeneous, incompressible deformation field.

3.1.3 Volumetric Compression Tests

Due to the high melt viscosity and the resulting manufacturing difficulties it is common for fluoropolymers to contain a small amount of porosity. To examine the influence of porosity on the response of the PTFE material examined in this work was a limited set of volumetric compression experiments performed. In these experiments, a small cylindrical specimen was constrained in a fixture and compressed. The volumetric
response of the samples with applied pressure was then determined by measuring the force-displacement response with applied deformation. The tests were performed at a slow deformation rate, $6.7 \times 10^{-5}$/min, during both loading and unloading.

### 3.1.4 Multiaxial Small Sample Punch Tests

In a final test series, 15%-vol fiberglass-filled PTFE, small disc-shaped specimens measuring 6.4 mm in diameter and 0.5 mm in thickness, were machined from the raw material. Mechanical tests were then performed using a closed-loop servo-hydraulic test system equipped with an environmental chamber. Specimens were tested by indentation with a spherical head punch at a constant punch displacement rate of 0.5 mm/min, both at 20°C and at 200°C. These experiments were performed in order to probe the multiaxial deformation response through the measured force-displacement response of the punch head.

### 3.2 Plastic Memory Effect Tests

Kletschkowski et al. (2000) published the results of thermo-mechanical cyclic tests on a 5% fiberglass, 5% MsO$_2$ PTFE compound. These tests exhibit the complex behavior of PTFE, in which the phenomena of stress relaxation, viscoelastic strain recovery and permanent (unrecoverable) strain can be observed. In particular, it appears that the magnitude of the recoverable strain is dependent on the number of thermo-mechanical cycles and that the recoverable strain may reach a saturation point, which they refer to as the "plastic memory effect" or PME. In one of their cyclic loading tests, see Figures 16 and 17 of their paper, they subjected a specimen (58 mm by 5 mm by 2 mm) to five 5000-second repetitions of the following thermo-mechanical loading schedule: (1) the specimen was first loaded in uniaxial tension to a strain of 0.15 at a strain rate of 0.10/min, at room temperature, and then held at that strain for 2,500 seconds; (2) ten minutes after the specimen was initially stretched to a strain of 0.15, a 100°C thermal cycle was applied to the specimen; (3) the specimen was then completely unloaded and allowed to creep for about 2,500 seconds; (4) while the specimen was unloaded (and creeping), another 100°C thermal cycle was applied.

### 3.3 Analytical

The capability of the new DNF-model to predict the response of the fiber filled PTFE was evaluated by comparing the model predictions with the experimental data discussed above. The first step in this effort was to calibrate the model to the uniaxial tensile, compressive, and volumetric compression data. In this
work we used a combination of known stress-strain data from the literature for PTFE (Ebnesajjad, 2000) and the experimentally determined stiffness from the small punch tests to extract the temperature dependence of the shear modulus (Kurtz et al., 2002).

To find the material parameters we used the same approach as in our earlier work (Bergström et al., 2003): first, an initial estimation of the material parameters was made using a combination of a graphical technique (Bergström and Boyce, 2001) and a trial-and-error approach. Then, a specialized computer program based on the Nelder-Mead simplex minimization algorithm was used to iteratively improve the correlation between the predicted data set and the experimental data. The quality of a theoretical prediction, and therefore of the chosen material parameters, was evaluated by calculating the coefficient of determination ($r^2$) (Bergström et al., 2003). The reported material parameters are from the set having the highest $r^2$-value.

After the optimal material parameters were found, the same material parameters were then used to simulate the small punch tests at the two temperatures. These validation simulations were performed in order to examine the capability of the DNF-model to predict multiaxial deformation states at different temperatures. The small punch simulations were performed using the ABAQUS/Standard (ABAQUS, Inc) finite element package (HKS, Inc., 2002). The simulations were based on an axisymmetric representation of the punch test with 360 quadratic triangular elements (CAX8H) to represent the specimen and loading geometry (see the inset in Figure 15). The simulations were performed using a friction coefficient of 0.01 between the PTFE sample and die and punch.

In addition, we simulated the thermo-mechanical, cyclic loading tests presented by Kletschkowski, et al., in 2002. Their tests were conducted on a PTFE compound constituted of 90% PTFE, 5% fiberglass and 5% MoS$_2$. We calibrated this PTFE compound using uniaxial tension tests presented by the authors (not reproduced in this paper).

4 Results

4.1 Experimental

The thermomechanical behavior of unfilled PTFE when tested in uniaxial tension at different temperatures has been reported in the literature (Ebnesajjad, 2000) and is summarized in Figure 2 illustrating that both the material stiffness and the viscoplastic response are strongly dependent on the temperature. The influence of applied temperature on the Young’s modulus is summarized in Figure 3 showing that the dependence
of the Young’s modulus or shear modulus on temperature for unfilled PTFE can be represented by the exponential representation given in Equation (2): 

\[ E(\theta) = E_0 \exp((\theta_0 - \theta)/\theta_{base}), \]

where \( E_0 = 365 \text{ MPa}, \) and \( \theta_{base} = 100^\circ \text{C}. \) This representation has been used in this work to also represent the behavior of the fiber glass filled PTFE. Here, the parameters \( E \) and \( \theta_{base} \) were obtained from the Young’s modulus obtained from the uniaxial tests, and from the extracted Young’s modulus obtained from the initial slopes of the small punch force-displacement response at 20\(^\circ\)C and 200\(^\circ\)C (Kurtz et al., 2002). As was discussed in Section 2, the exponential form of this expression can be directly inserted in Equation (1) to capture the temperature dependence of the shear modulus.

The behavior of the material in uniaxial tension and compression is shown in Figure 4 illustrating a stiffer response in compression than in tension. The rate of stress relaxation of the material is exemplified in Figure 5. The figure shows that the stress response initially decays very rapidly; after 10 minutes the stress decays down to 65% of its initial value.

The small strain response, including both loading and unloading, is shown in Figure 6. It is clear that the material starts to undergo viscoplastic deformation at strains below 1%. It is also interesting to note the significant amount of hysteresis and irreversible plastic strain at these small strain levels.

The experimentally determined volumetric compression response is shown in Figure 7, illustrating both
Figure 3: Influence of temperature on the Young’s modulus of unfilled PTFE.

Figure 4: Comparison between experimental data in uniaxial tension and uniaxial compression.
Figure 5: Stress relaxation behavior of fiberglass-filled PTFE at a strain level of 0.01, after a strain rate ramp of 0.5/s.

Figure 6: Small strain loading and unloading behavior of filled PTFE.
elastic and viscoplastic components of the response.

Figure 7: Triaxial (hydrostatic) compression behavior of filled PTFE at an applied strain rate of $1.1 \times 10^{-6}$/s.

The small punch behavior of the fiberglass filled PTFE is shown in Figure 8. The response shown in the figure is qualitatively very similar to other thermoplastics (Bergström et al., 2002). In the experiments, the specimen is initially elastically deformed, then viscoplastically bent, and finally biaxially stretched. The solid squares at the end of the two experimental lines shown in the figure corresponds to the ultimate failure points of the specimens. The inset in the figure shows a photograph of the final failed specimen from the test that was performed at 20°C.

The thermo-mechanical loading history carried out by Kletschkowski et al. (2000) is depicted in Figure 9. The strain and temperature are plotted as functions of elapsed time during the test, which consisted of five major loading and unloading, and ten 100°C thermal cycles. It is apparent that there is a permanent (unrecoverable) strain, which remains constant during all five cycles, (i.e., each time the specimen is unloaded, the strain falls initially to about 13%). However, the magnitude of the recoverable strain appears to decrease with the number of thermo-mechanical cycles. The stress versus strain response of the specimen is reproduced in Figure 10. The effect of the decreasing recoverable strain is manifested as a shrinking hysteresis loop. Note that the unloading curves appear to overlap, regardless of the number of cycles.
Figure 8: Experimental results from the small punch tests at an applied punch displacement rate of 0.5 mm/min.

Figure 9: Thermo-mechanical loading sequences of Kletschkowski et al. (2000).
4.2 Analytical

Values for the required material parameters for the filled PTFE material are given in Table 1. These parameters were obtained using the technique discussed in Section 3.3. Note that these parameters were used in all simulations discussed in this section. A direct comparison between the experimental and the predicted data using the calibrated Dual Network Fluoropolymer (DNF) model is shown in Figures 11 to 16. The $r^2$-values for the simulations ranged between 0.870 for the uniaxial small-strain cyclic loading tests to 0.945 for the triaxial compression tests. For the applications motivating this work, compression of a ring gasket seal, this variation in $r^2$ is acceptable.

Figure 11 shows the predictions for the small strain tension data. As is seen in the figure, the model captures the observed strain-rate dependence and hysteresis at small strains reasonably well.

The result from simulating the stress relaxation test is shown in Figure 12. It is clear that the model accurately captures the stress magnitude and the rate and amount of stress relaxation.

The predictions of the intermediate strain data in tension and compression are shown in Figure 13, demonstrating that the model captures the different flow behavior in tension and compression very well.

The volumetric response is shown in Figure 14. Both the bulk modulus and the volumetric flow are
Table 1: Material constants used in the simulations.

<table>
<thead>
<tr>
<th>Material Constant</th>
<th>Value</th>
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<tbody>
<tr>
<td>$\mu_A$</td>
<td>6.37 MPa</td>
</tr>
<tr>
<td>$\chi_{lock}$</td>
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<td>$\kappa$</td>
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<td>$\theta_{base}$</td>
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<td>$m$</td>
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<td>$n$</td>
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<td>$\tau_{base}$</td>
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<tr>
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<td>$b$</td>
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</tr>
<tr>
<td>$\sigma_0$</td>
<td>13.4 MPa</td>
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</tbody>
</table>

Figure 11: Comparison between experimental data and predicted behavior in uniaxial tension at different strain rates ($T = 20^\circ C$, applied strain rates: $6 \times 10^{-3}/s$ and $6 \times 10^{-4}/s$).
Figure 12: Comparison between predicted and experimental stress relaxation results.

Figure 13: Comparison between experimental and predicted behavior in uniaxial tension and compression.
Figure 14: Triaxial compression response at an effective applied strain rate of 0.001/s.

The results from the small punch simulations are shown in Figures 15 and 16, exhibiting a direct comparison between the experimentally determined force versus displacement response at 20°C and at 200°C. The small punch test was simulated by implementing the PTFE model as a user subroutine in the ABAQUS finite element program (HKS, Inc., 2002), and creating a finite element representation of the experimental setup. Figures 15 and 16 demonstrate that the DNF-model captures very well the experimentally observed response at 20°C. The model does a reasonably good job of predicting the small punch behavior of 200°C.

The results of the simulation of the five-cycle thermo-mechanical PME tests of Kletschkowski et al. (2000) are shown in Figures 17 and 18. These simulation results are to be compared to the experimental results shown in Figure 17 and 18. The new constitutive model appears to to replicate the plastic memory effect (PME) well and can provide a tool for further understanding of the mechanisms responsible for the PME.

5 Discussion

The thermomechanical behavior of fluoropolymers is very complex. The constitutive relationship is non-linear, strain-rate dependent, elastic-viscoplastic, and temperature dependent. These features present a
Figure 15: Comparison between experimental and predicted load vs. displacement of a small sample punch test performed at 20°C.

Figure 16: Load vs. displacement of a small sample punch test performed at 200°C.
Figure 17: Plot of strain and temperature during simulation of plastic memory effect (PME) test.

Figure 18: Stress-strain response using new DNF model to simulate PME tests.
significant challenge to development of a computational model to predict of constitutive response. In this work we have studied 15 vol% fiberglass filled PTFE and 5%-vol fiberglass, 5% MsO$_2$ PTFE materials using uniaxial tension, uniaxial compression, uniaxial stress relaxation, triaxial compression, small sample punch, and cyclic loading thermo-mechanical tests. Motivated by earlier models for elastomers and glassy polymers (Bergstr"om and Boyce, 1998; Arruda and Boyce, 1995), we have developed a constitutive framework capable of accurately capturing all the experimentally observed characteristics using a single set of material parameters. The modeling effort has focused on the physics of the deformation mechanisms by establishing the framework and equations necessary to model the behavior on the macroscale. The use of a constitutive model for a given material requires a calibration step where the material specific parameters are determined. A variety of numerical approaches can be employed to determine the required material parameters. In this study we applied a semi-automatic optimization algorithm to find the most representative parameters.

Of greater importance than how the material parameters were determined is how well the model represents the governing micromechanisms, and ultimately, how accurately the model can predict continuum deformation histories. In this work we have evaluated and quantified the performance of the proposed model by comparing the predictions with the experimental data for 15 vol% glass fiber filled PTFE, and a % fiberglass, 5% MsO$_2$ PTFE compound. These direct comparison have shown that the new model can accurately predict the experimentally observed behavior in monotonic and cyclic uniaxial loading, cyclic thermal loading, cyclic thermal loading, and in multiaxial deformation states, over a broad range of temperatures.

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