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A constitutive model for predicting the large deformation thermomechanical behavior of fluoropolymers

J.S. Bergström [a,*], L.B. Hilbert Jr. [b]

[a] *Exponent, Inc., 21 Strathmore Road, Natick, MA 01760, USA*
[b] *Exponent, Inc., 149 Commonwealth Drive, Menlo Park, CA 94025, USA*

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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.

Keywords: Constitutive modeling; PTFE; Fluoropolymer; Finite element simulation; Large strain; Time-dependence; Experiments

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,

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[*] Corresponding author. Tel.: +1 508 652 8514; fax: +1 508 647 1899.
E-mail addresses: jorgen@alum.mit.edu (J.S. Bergström), bhilbert@exponent.com (L.B. Hilbert Jr.).
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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 ethylenetetrafluorethylene 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 nonlinear 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 Krempl, 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 gen-