

Nonlinear Viscoelastic Response of Thermoplastic–Elastomer Melts

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Abstract. Observations are reported on thermoplastic elastomer (ethylene-octene copolymer) melt in small-amplitude shear oscillatory tests and start-up shear tests with various strain rates in the interval of temperatures between 120 and 210 °C. Based on the concept of heterogeneous non-affine polymer networks, constitutive equations are developed for the thermo-mechanical behavior of a melt at three-dimensional deformations with finite strains. Adjustable parameters in the stress-strain relations are found by fitting the experimental data. The model is applied to the analysis of Poiseuille flow. The effects of temperature and pressure gradient on the steady velocity profile are studied numerically.

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1 Introduction

This paper deals with the experimental investigation and constitutive modeling of the nonlinear thermo-viscoelastic response of thermoplastic-elastomer (TPE) melts at three-dimensional deformations with finite strains. Modeling the time-dependent behavior of polymer melts has been a focus of attention in the past three decades. Among constitutive equations for the viscoelastic and viscoplastic responses of polymer melts, it is worth mentioning (i) the Leonov model [1], (ii) the Johnson–Segalman model [2], (iii) the Phan Thien–Tanner model [3], (iv) the Wagner model (a modification of the

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K–BKZ constitutive equations) [4], (v) the Giesekus model [5], (vi) the finitely extensible nonlinear elastic (FENE) network model [6], (vii) the pom–pom model [7], (viii) the reptation model with incorporation of segmental stretching [8], and (ix) molecular stress function model [9], to mention a few.

The present study focuses on the nonlinear thermo-viscoelastic behavior of a thermoplastic elastomer (ethylene-octene random copolymer) melt in conventional (i) oscillatory shear tests with small amplitudes and (ii) start-up shear tests with constant strain rates at various temperatures. Rheology of ethylene-octene copolymer melts has attracted substantial attention in the past decade (see [10]– [19]) for two reasons. First, these polymers with large concentrations of higher olefin comonomers (above 20 wt.-%) are widely used as rubber modifiers for thermoplastics [15]. Secondly, ethylene copolymers produced by metallocene catalysis have relatively low polydispersity and contain long chain branches that strongly affect their properties. In particular, (i) the zero-shear viscosity and (ii) the apparent flow activation energy of polyethylenes with long-chain branches noticeably exceed those of conventional polyethylenes with similar molecular weights.

There are two ways to model viscoelasticity of a polymer melt. According to the first (which goes back to [20,21]), the melt is treated as a transient network of strands, and its time-dependent response is associated with rearrangement of chains in the network (separation of active strands from temporary junctions and attachment of dangling chains to the network). According to the other approach [2,3], the melt is thought of as a permanent, but non-affine network of chains. The non-affinity means that junctions between chains slide with respect to their reference positions under deformation, and the deformation gradient for sliding (plastic flow) of junctions differs from that for macro-deformation. Following the latter concept, we treat a thermoplastic-elastomer melt as an incompressible, inhomogeneous, non-affine network of chains linked by junctions (entanglements and physical cross-links). Heterogeneity of the network is induced by local density fluctuations. To account for the inhomogeneity, a melt is thought of as an ensemble of meso-regions with various activation energies for sliding. Distribution of meso-regions is assumed to be independent of temperature and mechanical factors.

Stress–strain relations for a polymer melt and kinetic equations for sliding (plastic flow) of junctions are developed by using the laws of thermodynamics. The conventional method of derivation is grounded on the assumption that the plastic vorticity tensor vanishes. A novelty of our approach is that the constitutive equations are deduced without any hypothesis regarding this tensor.

An advantage of the constitutive model is that it involves a small number of adjustable parameters (5 for an isothermal loading and 8 for arbitrary non-isothermal deformations) with transparent physical meaning. These quantities are determined by fitting the experimental data in shear tests with small and large strains. Not more than 3 constants are found by approximation of observations in each test, which ensures that material parameters are determined with a high level of accuracy. Ability of the constitutive equations to describe the mechanical response of TPE melts is ex-