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Thermo-viscoelastic response of nanocomposite melts

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Abstract

Observations are reported in shear oscillatory tests with small strains (the frequency-sweep mode) on a hybrid nanocomposite melt [thermoplastic elastomer (ethylene–octene copolymer) reinforced with various concentrations of montmorillonite nanoclay] at temperatures ranging from 150 to 210 °C. A constitutive model is developed for the viscoelastic behavior of a nanocomposite melt at arbitrary three-dimensional deformations with small strains. The melt is treated as an inhomogeneous, permanent polymer network with sliding junctions (entanglements and physical cross-links at the surfaces of nanofiller). It is assumed that macro-deformation induces sliding (plastic flow) of junctions between strands with respect to their reference positions, and the strain energy of the network depends on strain tensors for elastic and plastic deformations. Stress–strain relations are derived by using the laws of thermodynamics. These equations involve four adjustable parameters that are found by fitting the observations. It is demonstrated that (i) the governing equations correctly reproduce the experimental data and (ii) the material parameters change consistently with temperature and concentration of filler.

Keywords: Thermoplastic elastomer; Hybrid nanocomposite melt; Shear oscillations; Thermo-viscoelasticity; Constitutive equations

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1. Introduction

This paper deals with experimental investigation and constitutive modeling of the linear viscoelastic response of hybrid nanocomposite melts (polymer melts reinforced with nanoclay platelets and their stacks). Experimental and theoretical analysis of the rheological behavior of nanocomposite melts has been a focus of attention in the past decade. This may be explained by two reasons: (i) rheological tests provide a convenient and reliable tool to characterize polymer/clay nanocomposites and (ii) observations in these tests are exquisitely sensitive to concentration, size, and distribution of particles, as well as to structural changes in morphology of the host matrix driven by the presence of nanofiller [1–4]. Observations on the linear viscoelastic response of polymer/organically modified silicate melts have been reported in a number of studies, see, for

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example, experimental data on polyamide [5–8], polycarbonate [9,10], polyethylene [11–14], polypropylene [15–20], and polystyrene [21–24].

Unlike the above polymers, relatively small attention has been paid to the rheology of thermoplastic elastomers filled with nanoclay [25–29]. Thermoplastic elastomers provide an important class of polymers that combine mechanical properties of rubbers (large deformations without changes in the internal structure) with high-speed processability and recyclability of thermoplastics [30]. The aim of the experimental part of this work is to study the linear thermo-viscoelastic response of a thermoplastic elastomer (TPE) (ethylene–octene copolymer) reinforced with montmorillonite (MMT) nanoclay in a wide range of temperatures and concentrations of filler. The interest to rheological properties of TPE/MMT hybrid nanocomposites may be explained, among other reasons, by rapid growth of the area of applications of these systems as implant materials for soft tissue replacement and reconstruction [31].

Observations on nanocomposite melts in shear oscillatory tests with small amplitudes reveal a number of intriguing phenomena. In particular, this study concentrates on transition from the conventional liquid-like behavior to the so-called pseudo-solid-like response with the growth of nanofiller content.

An increase in filler loading induces substantial evolution of the dependencies of storage, G', and loss, G'', moduli of a nanocomposite melt on frequency of oscillations ω. The functions $G'(\omega)$ and $G''(\omega)$ of a neat polymer melt are proportional to ω^2 and ω, respectively, in the interval of low frequencies (between 0.1 and 1 rad/s). An increase in concentration of nanoclay alters these scaling dependencies, and the quantities G' and G'' become practically independent of frequency at relatively small ω. This transformation is conventionally referred to as formation of a low-frequency plateau, or transition to a pseudo-solid behavior. The storage and loss moduli corresponding to the plateau, as well as the region of frequencies, within which the moduli remain constant, monotonically grow with concentration of nanofiller. This phenomenon is observed on a number of hybrid nanocomposites melts such as polyamide [6,8], polycarbonate [10], polyethylene [13,14], polypropylene [17–19], and polystyrene [21], to mention a few. In another form of presentation of experimental data, it is revealed as disappearance of the Newtonian plateau and strong reduction of the complex viscosity with ω at relatively low frequencies [17]. Surprisingly, we found no publications where observations were reported on formation of a low-frequency plateau in TPE/MMT nanocomposite melts. The experimental part of this work focuses on thorough investigation (in a relatively wide interval of temperatures) of transition to the pseudo-solid-like response with increase in nanoclay concentration.

Several physical models have been proposed in the past decade for the onset of low-frequency plateaus on the graphs $G'(\omega)$ and $G''(\omega)$. Most of them associate this phenomenon with (i) transition from a homogeneous dispersion of exfoliated clay platelets in the host matrix to a heterogeneous dispersion of partially intercalated stacks when the filler loading exceeds its percolation threshold [7], (ii) agglomeration of stacks in particulate domains, where free rotation of clay tactoids is hindered by the adjacent ones [16], and (iii) formation of a secondary network of weakly agglomerated particulate domains bridged by polymer chains [15]. Not arguing the validity of these hypotheses, it is worth emphasizing that they can serve for qualitative description only, while a way for their application to the quantitative analysis of experimental data remains rather unclear. The theoretical part of this study concentrates on derivation of a novel constitutive model that can adequately describe the pseudo-solid response of hybrid nanocomposite melts at small strains.

The objective of this work is fourfold: (i) to report observations in small-amplitude shear oscillatory tests on TPE/MMT nanocomposite melts with various concentrations of nanoclay in a wide interval of temperatures, (ii) to develop constitutive equations for the linear viscoelastic response of nanocomposite melts at arbitrary three-dimensional deformations, (iii) to find adjustable parameters in the stress–strain relations by fitting the experimental data, and (iv) to evaluate the effects of temperature and filler content on material parameters in the governing equations.

The exposition is organized as follows. Observations in shear oscillatory tests with small amplitudes on ethylene–octene copolymer reinforced with organically modified montmorillonite nanoclay are presented in Section 2. Constitutive equations for the linear viscoelastic response of a nanocomposite melt are developed in Section 3 by using the laws of thermodynamics. The stress–strain relations are simplified for shear oscillatory tests, and explicit expressions are derived for the storage and loss moduli as functions of frequency. Experimental parameters in the governing equations are found in Section 4 by fitting observations. The effects of