Mechanics Research Communications xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Mechanics Research Communications

journal homepage: www.elsevier.com/locate/mechrescom

Micromechanics of semicrystalline polymers: Towards quantitative predictions

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ARTICLE INFO

Article history:
Received 15 October 2015
Accepted 7 January 2016
Available online xxx

Keywords:
Semicrystalline polymers
Micromechanics
Composite inclusion model
Yield kinetics
Creep

ABSTRACT

An initially qualitative two-phase elasto-viscoplastic micromechanical model for the mechanical performance of semicrystalline materials has previously been developed. In the last decade, a series of extensions to this model have been aimed towards quantitative predictions of the response of semi-crystalline polymers based on their microstructure. These developments included extensive experimental characterization and modelling of the yield kinetics, time-to-failure, creep and thermal shrinkage and expansion. This paper gives an overview of the route from the initially qualitative model to a model that quantitatively captures these complex aspects of the mechanical response of a semicrystalline polymer.

1. Introduction

The mechanical response of a polymer material, including the mode of failure and the time-scale on which it occurs, is strongly influenced by the processing conditions. This is particularly true for semicrystalline polymers [e.g. 1,2] in which structural features, such as the degree of crystallinity, crystal type, size and orientation, that strongly influence their mechanical properties, may vary drastically depending on subtle details of the manner in which the polymer is shaped into the final product. For example, shear flow significantly accelerates crystallization kinetics by increasing the amount of nuclei and generates an anisotropic morphology by inducing orientation. Therefore, during processing of a material often an oriented microstructure is formed, leading to anisotropic properties. This anisotropy is intentionally created in fibre spinning, and film casting or film blowing, however, for injection-moulded products, anisotropy is usually an artefact of the processing conditions required to obtain an optimally shaped product. To improve product performance for any of these processes, a fundamental and quantitative understanding of how anisotropic properties, including yield and failure kinetics, depend on the (oriented) structure is required.

Several experimental and modelling studies have focused on understanding the viscoplastic behaviour of semicrystalline polymers [e.g. 3–8]. Macroscopic and phenomenological constitutive models for solid polymers have been successfully developed for rapid and efficient numerical evaluation of the performance of polymer products [e.g. 9–11]. These constitutive models capture the time, stress and temperature-dependent response of polymers, including the effect of their thermo-mechanical history. A micromechanical model that describes the macroscopic response as a function of the morphological structure and constitutive properties of the constituents has the potential to form a predictive tool for the macroscopically anisotropic properties of a semicrystalline polymer with an arbitrary processing-induced microstructure.

Finite-element modelling may be used to describe the mechanical behaviour of a semicrystalline polymer with a known microstructure, i.e. isotropic (spherulitic) or oriented [e.g. 12–14]. These approaches are generally computationally demanding and required cumbersome meshing of the microstructure. Alternatively, various mean-field models have been developed for semicrystalline polymers, such as [3,5,8,15–23]. These micromechanical models often aim at predicting the effective elastic properties based on the polymer's microstructure and in some cases focus on the more complicated yield behaviour as well. An elasto-viscoplastic micromechanical model for semicrystalline polymers was developed by the authors [24–26]. The basic

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http://dx.doi.org/10.1016/j.mechrescom.2016.01.002
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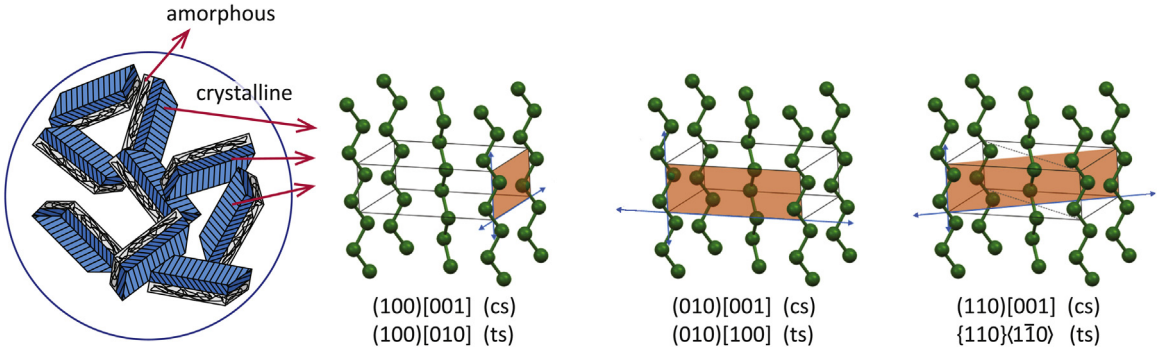

Fig. 1. An aggregate of *composite inclusions* (left) and the six physically different types of slip systems in a polyethylene crystal (right), with "cs" denoting chain slip and "ts" indicating transverse slip.

element in this model is a layered two-phase structure, comprising both a crystalline and an amorphous domain as developed by Lee et al. [5,15] for rigid viscoplastic semicrystalline materials. Initially, the application of these micromechanical models has been mostly limited to systems with a spherulitic and thereby macroscopically isotropic structure (whereas most polymer products have an intrinsically oriented structure) and was aimed at obtaining a qualitative description of the mechanical response [e.g. 14,24,27]). Further research has focused on improving the quantitative abilities of the multiscale micromechanical model, in particular for the stress-dependence of the rate of plastic deformation, i.e. the yield kinetics [28–30]. Recent efforts were successful in providing a quantitative description of macroscopic yield and failure kinetics, also for oriented material [31,32]. In this paper, an overview is given of the development of the so-called *composite inclusion* model for semicrystalline polymers from first being a qualitative model, towards a model that quantitatively predicts the response of these materials.

2. A qualitative model for semicrystalline polymers

2.1. Composite inclusion model

A rigid-plastic mean-field micromechanical model for semicrystalline polymers, referred to as the *composite inclusion* model, was proposed in 1993 in the pioneering work of Lee et al. [5,15] and was used to predict the texture evolution in these materials. The basic element in this model was a two-phase layered structure consisting of a crystalline and an amorphous phase. This concept was later extended to elasto-viscoplastic behaviour by Van Dommelen et al. [24]. In this concept, the response of the semicrystalline material is modelled as an average of an aggregate of these two-phase composite inclusions (see Fig. 1). Within each composite inclusion, the two phases are assumed to be kinematically compatible and in equilibrium across the interface and a hybrid local–global interaction law is used to relate the volume-averaged mechanical behaviour of each composite inclusion to the imposed boundary conditions for an aggregate of inclusions.

Since the crystalline domain consists of regularly ordered molecular chains, in [24] the response of these domains was modelled as anisotropic elastic in combination with plastic deformation governed by crystallographic slip on a limited number of slip systems and for which a rate-dependent crystal plasticity model was used. It should be noted that in contrast to metallic materials, for polymer crystals, the various slip systems are usually physically distinct (for example, the slips systems of a polyethylene crystal are shown in Fig. 1) and therefore have different properties. The amorphous phase of semicrystalline polymeric material consists of an assembly of disordered macromolecules, which are morphologically constrained by the neighbouring crystalline lamellae. In [24], the elastic deformation of the amorphous domains was modelled by a generalized neo-Hookean relationship in combination with a viscoplastic relation and an eight-chain network model to account for orientation-induced strain hardening. For both the slip systems and the amorphous domains, the viscoelastic behaviour was modelled with a power law relation.

2.2. Application to HDPE

This elasto-viscoplastic model was used to describe the macroscopic response of spherulitic (and therefore initially isotropic) high density polyethylene (HDPE), including the effect of crystallinity and to study micromechanical deformation mechanisms. In particular, the intra-spherulitic deformation mechanisms were studied in a multi-scale effort in [27] and the effect of an oriented microstructure in extruded HDPE was qualitatively modelled in [25].

3. Towards quantitative predictions

3.1. Yield kinetics of isotropic HDPE

The next phase in the development of the composite inclusion model was directed towards the quantitative prediction of the yield and post-yield behaviour in semicrystalline polymers during large deformations at different strain rates. A critical factor for this is the stress-dependence of the rate of plastic deformation, the yield kinetics. The kinetics of the macroscopic plastic flow strongly depend on the slip kinetics of the individual crystallographic slip systems. Therefore, an accurate quantitative prediction requires a proper description of the rate-dependence of slip along crystallographic planes. As a first step in achieving this goal, the previously used viscoplastic power law relation was replaced with an Eyring flow rule, which more closely matches the macroscopically observed response. The re-evaluation of the slip kinetics was performed using a combined numerical/experimental approach and the refined slip kinetics were then validated for uniaxial compression data of isotropic HDPE, for different strain rates [29]. A double yield phenomenon was found in the model predictions and was related to morphological changes that induce a change of deformation mechanism, see Fig. 2. In the case of polyethylene, such a double yield point has also been observed experimentally during both tensile and compressive deformation modes. In literature, several possible mechanisms have been proposed to explain this behaviour, among which different deformation processes for the first and second yield point, often associated with fine slip and coarse slip [33–36]. Even though the composite inclusion model considers only fine slip, it mimics this complex behaviour, where

Please cite this article in press as: J.A.W. van Dommelen, et al., Micromechanics of semicrystalline polymers: Towards quantitative predictions, Mech. Re. Commun. (2016), http://dx.doi.org/10.1016/j.mechrescom.2016.01.002