Three-dimensional constitutive model for the description of high molecular weight semicrystalline polymers over a large range of temperatures and strain rates

Application to Ultra High Molecular Weight PolyEthylene

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Abstract. Semi-crystalline polymers, and more particularly high molecular weight semi-crystalline polymers, exhibits interesting properties such as wear and impact resistance which contributes to their spreading into several industries and applications. However, because they have very long chains and exhibit high viscoelastic mechanical behavior, they are difficult to process. It requires high temperature, close to melting temperature, and important compression strength to arrange the chains. However, such process lack accuracy and better understanding of the thermomechanical behavior is needed to improve it. Thus, a three-dimensional model based on the evolution of the microstructure during the plastic deformation have been developed with relative good agreement with experimental results from the literature.

1 Introduction

Polymers, and more especially semi-crystalline polymers, exhibit complex thermomechanical behavior highly dependent on their micro-structure (amorphous versus crystalline phase arrangement) [1]. Although they are widely used, the physics behind their deformation is still not well understood leading to strong misinterpretation of their thermomechanical behavior and early fracture during their use. A way to overcome these difficulties is to study the deformation mechanisms and to develop a numerical model according to these mechanisms.

The microstructure of polymers, and more particularly high molecular weight semicrystalline is characterized by very long macromolecular chains which participate at the same time to the crystalline lamellae, tie molecules and macromolecular network [2]. Such polymers exhibits three stages of deformation. the first stage corresponds to the initially rigidity of the material. Elongation of the tie molecules and dislocation of the crystal structure is observed. At the end of this stage, the crystal starts to break apart leading to non homogeneous crystal sizes [3]. The second stage corresponds to the plastic deformation of the material. From the microstructural viewpoint, the crystalline lamellae undergo fibrillation process starting from the periphery. This mechanism increases the length of the tie molecules which become fibrils. Moreover, because of the applied stretching, rotation and alignment of the crystal blocks in the loading direction is observed. In the last stage of deformation, important stretching of the amorphous fibrils in the loading direction happens leading to locking phenomena of the polymer chain segments.

To represent such behavior, several authors [4–7] developed numerical models based on the polymer physics. Most of these models have been developed for amorphous materials and, therefore, do not consider the particular microstructure of semi-crystalline polymers. Thus, extensive researches have been performed to better understand and predict the mechanical behavior of these materials. For example, Gueguen et al. [8] developed a yield point model for semi-crystalline polymers. The model is based on the formulation of the cooperative model [6]. By considering an effective volume and an effective energy for the polymer, it does not allow to represent fairly its crystalline structure. A way to achieve this, it is to consider, as separated entities but which act in strong interaction, fibrils and crystalline lamellae within the crystal network. From these observations, Humbert et al. [9] developed a numerical model which considers a scalable mechanical coupling between tie molecules/fibrils and crystalline lamellaes. With respect of the crystalline ratio, Humbert et al. [9] developed a non-parallel nor series model to predict the Young modulus for a wide range of polyethylene. Based on these observations, Deplancke et al. [10] developed a one-dimensional model to predict the thermomechanical behavior of high molecular weight polymers. It takes into account the evolution of the microstructure occurring during the plastic deformation of the polymer (transformation

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of the crystalline lamellae into fibrils). The model is in fair agreement with the experimental results in compression. However, as it is, the model scope is very narrow due to the one-dimensional formalism. To extend its range of applications, it is necessary to consider the deformation in every direction, ie. three-dimensional viewpoint. Therefore, based on the model of Deplancke et al. [10], we developed a numerical model using three-dimensional formalism. The formulation of this model will be explained in section 3, after a brief introduction of Deplancke et al.'s model [10] in section 2.

2 One-dimensional model for high molecular weight semi-crystalline polymers

As mentioned previously, the one-dimensional model developed by Deplancke et al. [10] takes into account the evolution of the polymer microstructure during its plastic deformation. The model can be separated into two separated networks acting in parallel: the scalable crystal network (intermolecular resistance) and the macromolecular network (network resistance) as illustrated by figure 1.
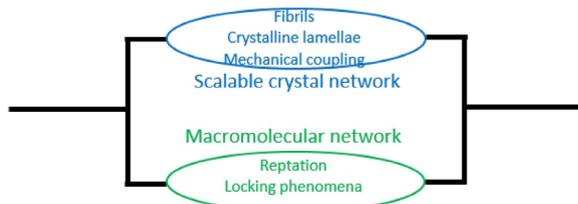

Fig. 1. Schematic representation of the numerical model.

The macromolecular network corresponds to the network resistance to the deformation due to the applied loading. The mechanisms involved are the disentanglement of the chain segments, ie. reptation, and their orientation in the loading direction. The formulation of these theories can be found in the works of de Gennes [11] for the reptation concept and in the works of Arruda and Boyce [7] for the orientational hardening and locking phenomena of the polymer chain segments.

The crystal network corresponds to the intermolecular resistance of the crystal structure. The stress and strain of the crystal structure are defined as function of the stress and strain of the fibrils (σ_f, ε_f) and crystalline lamellae (σ_c, ε_c) with respect of the crystalline ratio φ:

$$\sigma_{CN} = \varphi\sigma_c + (1-\varphi)\sigma_f \qquad (1)$$
$$\varepsilon_{CN} = \varphi\varepsilon_c + (1-\varphi)\varepsilon_f \qquad (2)$$

The mechanical coupling between crystalline lamellae and fibrils resulting from the fibrillation process is described through a proportional relationship between the stress of the crystalline lamellae and fibrils region, such as:

$$\sigma_c = k\sigma_f \qquad (3)$$

where k characterizes the mechanical coupling. To represent the evolution of the crystal structure during the plastic deformation, k evolves in function of the crystal's plastic deformation.

3 Three-dimensional constitutive modeling for high molecular weight semi-crystalline polymers

Using the three-dimensional formalism and because the macromolecular network and crystal network are in parallel, the total deformation gradient $\mathbb{F}$ is identical to the deformation gradient of the macromolecular network $\mathbb{F}_{MN}$ and the deformation gradient of the crystal network $\mathbb{F}_{CN}$.

The implementation of the macromolecular network from 1D to 3D model is usual and can be found in several works [12, 13]. Thus, no further explanation will be given here regarding the macromolecular network modeling.

Regarding the crystal network, its deformation gradient should account for the mechanical coupling between fibrils and crystalline lamellae with respect of the crystalline ratio. Thus, we propose the following relationship:

$$\mathbb{F}_{CN} = \mathbb{F}_f^{1-\varphi}\mathbb{F}_c^{\varphi} \qquad (4)$$

where $\mathbb{F}_f$ and $\mathbb{F}_c$ are the deformation gradient of the fibrils and the crystalline lamellae respectively. Moreover, we assume that crystalline lamellae and fibrils can deform elastically and plastically, such as $\mathbb{F}_i = \mathbb{F}_i^e\mathbb{F}_i^p$ where $i = f$, c. The relationship 4 decomposes the deformation in terms of fibrils' deformation and crystalline lamellae's deformation. However, no coupling between within the crystalline structure is described by this relationship. Deplancke et al. [10] introduces the scalable mechanical coupling through the stress (cf. 3). However, using 3D formalism and with the optic of using finite element simulations, introduction the coupling through a stress relationship is heavy in terms of computational cost. Thus, we define the mechanical coupling by the relationship:

$$\mathbb{F}_c = \left(\mathbb{F}_f\right)^{\zeta} \qquad (5)$$

where ζ defines the coupling between fibrils and crystalline lamellae. As k, ζ evolves with the plastic deformation of the crystal network.

From these definitions of the deformation gradients, the total stress of the crystal network $\mathbb{T}_{CN}$ is defined by:

$$\mathbb{T}_{CN} = (1-\varphi)\mathbb{T}_f + \varphi\mathbb{T}_c \qquad (6)$$

where the stress tensor of the fibrils $\mathbb{T}_f$ is defined using the hyperelatic model of Arruda and Boyce [7], and the stress tensor of the crystalline lamellae $\mathbb{T}_c$ is given by the Hooke's law.

4 Model Validation

The model has been validated using High Molecular Weight PolyEthylene under compressive unixial loading from the literature [10]. The results of the modeling are presented in figure 2. A good agreement is observed between experimental results and the numerical prediction over a wide range of strain rate.
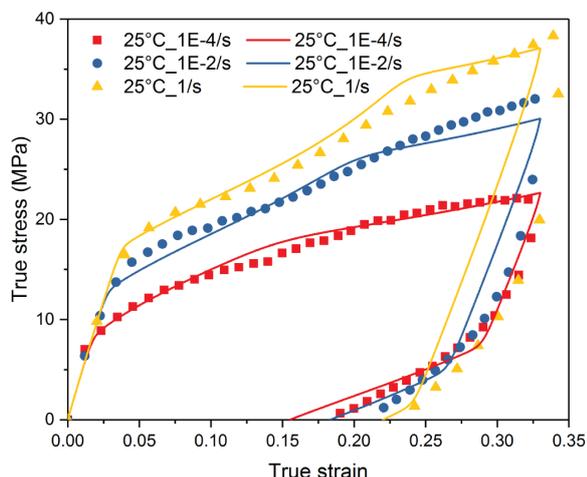

Fig. 2. Comparison between experimental results (dot) from Deplancke et al. [10] and the numerical predictions given by the three dimensional model (solid line).

This model have been introduced in the Finite Element software ABAQUS/Explicit through the writing of a VU-MAT subroutine. The aim is to simulate the high-velocity impact of a polymer particle against metallic substrate.

5 Conclusion

A three-dimensional model based on physical considerations have been developed to predict the thermomechani-cal behavior of ultra high molecular weight polymers. Improvement of the material properties are needed to obtain a better prediction of the thermal sensitivity of the model. However, the strain rate sensitivity is quite accurate over 4 decades. The next step of this work is to simulate the impact of micrometric polymer particle against a metallic substrate to improve the adhesion between the two materials. The aim of these model is to use it to predict the thermomechanical behavior of the particle during the deformation process.

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