Molecular Dynamics prediction of elastic and plastic deformation of semi-crystalline polyethylene

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ABSTRACT

The deformation of the spherulitic organization of a semi-crystalline polyethylene is not affine under tensile condition. The deformation is localized in the equatorial plane during the first steps of deformation [1]. The elastic and first steps of plastic deformation of a semi-crystalline polyethylene can be predicted by Molecular Dynamics method in this equatorial region. A fully-coupled model of amorphous and crystalline lamellae through the molecular chain path is proposed. The previous models were decoupled, the amorphous phase was strained in contact with a rigid crystalline phase or only the deformation of the crystalline phase was considered. A full-atom model is able to predict the correct amorphous and crystalline phases. It is built in order to be consistent with the physical parameters which characterize the semi-crystalline organization of a high density polyethylene formed with linear molecular chains. The isomolecular chains have a high molecular molecular weight (M =108 kdaltons) and a gyration radius consistent with experimental data. The crystalline content (α = 0.75) consists in crystalline lamellae (10 nm thick) in an orthorhombic phase (**a** = 0,74 nm, **b** = 0,493 nm, **c** = 0,254 nm) separated by amorphous phases (5 nm thick). The chain path goes through the crystalline and amorphous phases with multiple paths, including chain-foldings, large loops and thigh chain which connect the crystalline phases and are able to stress under tension the amorphous and crystalline phases [2]. The main orientation of chain folding [110] corresponds to the mechanisms of crystalline growth. The fraction of each contribution is chosen to be consistent with literature. A wide and a narrow distribution of thigh molecules are considered here, the literature is very poor to describe this physical parameter. The molecular models respect all the freedom degrees of this molecular organization and a Dreiding force-field is applied. The periodic 3D boundary model includes two lamellae and two crystalline phases to avoid an overconstrained model resulting from single amorphous and crystalline phases. The molecular system is then relaxed under NVT condition to reach the initial state.
A tensile experiment is applied on the molecular system perpendicular to the surface of the lamellae under constant load-rates with the DL_POLY code under NσT condition. A 1 fs time step is used for this full-atom model under a 0.1 nm.ps^{-1} strain-rate. The mechanism of deformation inside the amorphous and crystalline phases, and the force evolution, are detailed as a function of the microscopic deformation (fig. 1).
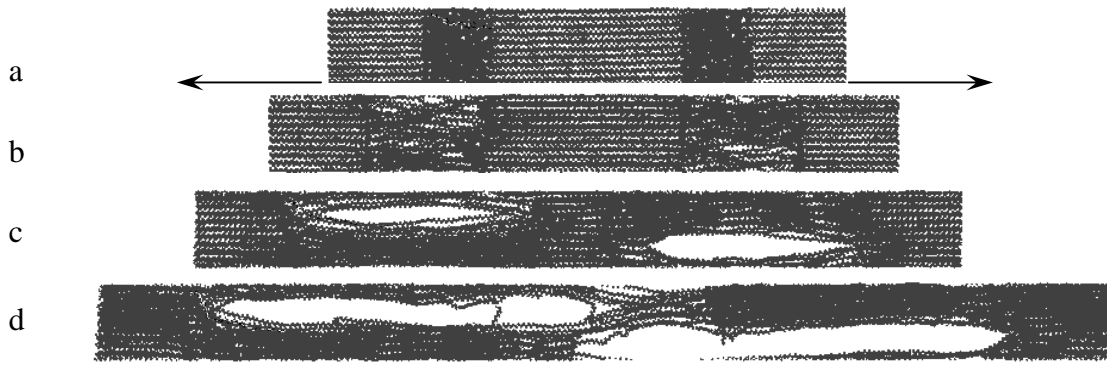
Figure 1: elastic and plastic deformation as a function of deformation under constant loading rate; a, état initial ; b, $\lambda = 0.2$; c, $\lambda = 0.5$; d, $\lambda = 1$

A cavitation appears very early in the amorphous phase for all the simulations, during the first steps of "elastic" deformation. This is consistent with experimental data [1]. This cavitation results from a topological constrain and doesn't depend on the thigh chain length distribution.

The solid-state rheology is deduced up to the yield-stress ($\varepsilon < 0.2$) and is compared to experimental data (fig. 2). The local analysis is possible experiments prove that the first steps of deformation are localized in the equatorial plane. Further deformation involves progressively other parts of the spherulites up to their poles and the predictions are not physically pertinent over that point. A wide distribution of chain length is consistent with experiments and implies that plastic deformation is activated very early.
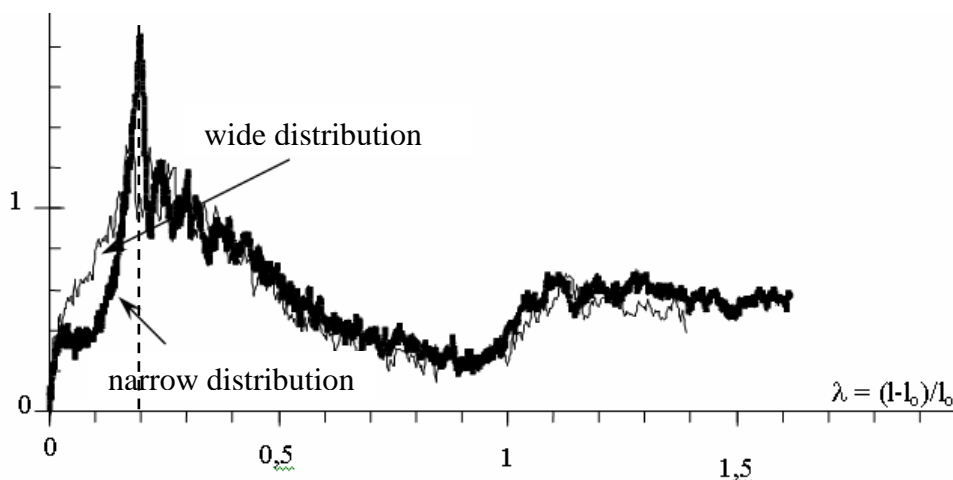

Figure 2 : stress-strain evolution up to the yield stress ($\lambda < 0.2$) for a wide and narrow length distribution of thigh molecules.

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