



Analysis of structural changes during plastic deformations of amorphous polyethylene

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ABSTRACT

Molecular dynamics (MD) simulations have been used to analyze yielding and stress-softening processes during stepped simple tensile loading of bulk amorphous polyethylene (PE) at temperatures (T_{def}) well below the glass transition temperature (T_g). Specimens formed by 20 linear chains of 1000 beads each (2×10^4 coarse grained $-\text{CH}_2-$ units), with energetics described by a united atom potential, were deformed at $T_{\text{def}} = 100\text{K}$. Configurations at axial strains (ϵ_{xx}) ranging from 0% to 30% were allowed to reach steady state equilibration. Subsequently, configurations in a time period of 5 ps were saved for analysis of their local structure. Local structural characteristics were analyzed using three methods: (i) a geometric description by computing the evolution of self and inter-chain entanglements, the number of bead contacts and the free volume, (ii) the method of Empirical Orthogonal Functions (EOF) to obtain a reduced description of the displacement field at each strain level and the vibration of each bead around its equilibrium position, and (iii) Hardy's method to compute the time averaged local stress tensor to obtain a detailed description of the distribution of internal forces. It was found that at early stages of deformation ($\epsilon_{\text{xx}} < 13\%$) the inter-chain entanglement continuously decreases while the self-entanglement showed no significant variation and no distinct patterning. Also the energy content in each eigenmode of the normalized displacement correlation matrix used in the EOF analysis is almost the same for a large portion of the frequency range regardless of the imposed axial strain level. Furthermore, distribution of the local pressure presented a positive expected value at the initial ($\epsilon_{\text{xx}} = 0\%$) configuration; the expected value continuously decreases toward the point where the axial stress peaks ($\epsilon_{\text{xx}} = 13\%$). The evolution of the number of loosely packed regions (quasi-defects), identified by a negative value of the local pressure, showed three distinct regimes: $\epsilon_{\text{xx}}(0\%–5\%)$, $\epsilon_{\text{xx}}(5\%–13\%)$ and $\epsilon_{\text{xx}}(13\%–30\%)$. The first regime corresponds to the fast nucleation of quasi-defects while the last one showed an inversion in the trend during the stress-softening regime with a moderate decreasing tendency. The three analyses show that the plastic deformation in this amorphous material commences with the nucleation of stress-induced defects without significant changes in the molecular degrees of freedom. Despite the chemical nature and inherent internal structure of the material under study, our findings support Argon et al.'s theory [1–4] as well as that of subsequent investigators [4,5] in that local structural rearrangements exist at locations where particles (beads) forming the material are loosely packed; these regions are termed the local shear transformation zones (STZ).

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1. Introduction

Glassy polymers are integral components in many modern industrial applications [6] because of their outstanding mechanical properties [7–9]. When subjected to large deformations, instead of failing abruptly, materials such as polycarbonate (PC) and poly-

methyl methacrylate (PMMA) show strain hardening for large strains [8], a valuable mechanical response required in many structural applications.

Even though glassy polymers, and in general polymeric materials, pervade many aspects of our everyday life, a deep understanding rooted in the micro-structure-property relationship of their behavior is still needed [10–13]. As the dimensions of structural components reach the nanometer scale in-homogeneities in the microstructural characteristics of the constituent materials start to dominate and deviations from the observed macroscopic

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behavior are expected [14–17]. In the quest for theoretical understanding of the mechanical properties of glassy polymers, molecular dynamics (MD) simulations have been used to elucidate relevant phenomena responsible for the observed macroscale properties of polymers and many other engineering materials. The challenging questions regarding the molecular origin of mechanical properties can be answered by having a suitable description of the deformation mechanisms involved when the material is subjected to a variety of external loading conditions (temperature, strain, strain rate, cooling rates etc.). Topical reviews of the progress in computational methods to study polymeric materials at nanoscale include Refs. [18–22,68].

Experimental results of uniaxial tensile/compressive tests have shown distinctive regimes in deformations of glassy polymers [20,21]. After an overshoot in the axial stress–axial strain curve the material experiences stress-softening at intermediate strains followed by strain hardening at large strains. MD simulations of tensile and compressive deformations of amorphous polymers have qualitatively reproduced macroscopic characteristics of these materials [18,19,23,24]. Details of the geometric description of deformation processes provided by these computations have allowed researchers to establish that conformational changes in linear amorphous polymers are mainly due to changes in the distribution of dihedral angles since changes in bond angles and bond lengths remain below 5% even at high strains [25].

For simple tensile tests on amorphous PE at different temperatures and constant strain rates, MD results of [23] suggest that deformations of linear glassy homo-polymers at large strains are mainly due to chain straightening of the constituent coiled macromolecules reflected in an increasing number of dihedral angles in the trans-conformation. It was also reported that as the strain rates increase ($\sim 10^{10}/s$) and for small and intermediate strain levels, the number of dihedral angles in the trans-conformation stays almost constant and equals that in the undeformed state. By using MD simulations of compression tests on the same polymeric material, Capaldi et al. [19] computed the variation of the percentage of angles in trans state with strain at different strain rates (5×10^9 , 1×10^9 , $5 \times 10^{10}/s$) and concluded that these changes are not significant prior to the strain hardening regime. The authors also stated that conformational changes in the dihedral angles do not play a major role in the mechanics of deformation during yielding. It is well known that conformational variations are required in order to allow changes in dimensions and shapes of coils and hence changes of the geometry of polymeric structures as a whole. Although the chain straightening mechanism is essential in describing the deformation process of glassy polymers it is still unresolved whether or not the same mechanism is responsible for developing plastic deformations at small and moderate strains [12,13].

Plastic deformation is a mass transfer process that changes shapes of a solid due to the applied external forces and the process involves irreversible relative atomic (molecular) motions [26]. During the solidification process and upon cooling to temperatures well below the melting point (T_m) or T_g , polymeric materials suffer a complete deactivation of the diffusional modes of mobility, i.e., non-existence of translational motion of polymer chains as a whole [8]. In this sense, low temperature plasticity in glasses at $T_{def} \ll T_g$ has to proceed via specific solid-like (solid state) rather than liquid-like structural rearrangements. At low temperatures only short scale motions without significant translational displacements of the conforming chains are allowed. Since thermal energy is insufficient to promote mass transfer, low temperature plasticity should be developed primarily through mechanical activation. Under this scenario, the two main characteristics regarding the plastic deformation in glassy polymers at $T_{def} \ll T_g$ are [13]: (i) molecular

motions responsible for mass transfer (plastic events) have to be small scale processes, and (ii) the source of mobility (plasticity carriers) is related to the nucleation and growth of new stress-induced structural defects that do not exist in the initial undeformed configuration. The second mechanism is similar to dislocation assisted plastic deformations in crystalline materials.

Plastic deformations in glassy materials have been explained as the nucleation and evolution of quasi-defects precipitated by the existence of a loose local environment (free volume) [1,27–29]. Similar characteristics in plastic processes occurring in both polymeric and non-polymeric glasses reveal that the plasticity of macro-molecular objects is not necessarily controlled by chain straightening or major conformational changes [30]. Mechanisms behind the relaxation process after the structure has been perturbed seem to be the same for different glasses regardless of their chemical nature (polymeric or metallic). Internal structure, packing and packing imperfections seem to control the evolution of structural defects in amorphous solids [31,32]. Intuitively it can be expected that the newly formed plastic events will be nucleated in the vicinity of loosely packed atomic configurations where the local density is smaller than that at other locations in the material. Different theories state that plastic deformations in amorphous materials might be due to the nucleation of local defects such as local shear displacements [1,4], linear defects such as dislocations [33] or free volume holes [27]. Due to similarities in local deformation patterns between amorphous materials with and without an internal structure, it is reasonable to expect that local structural rearrangements cause plastic events at the early stages of deformation rather than major changes in dimensions and shapes of the constituent polymer coils. Experiments have shown that uncoiling in polymer glasses is not important at early stages of deformation for $T_{def} \ll T_g$ and plays a role only after the system has reached the maximum axial stress [34,35].

In the present work, by using MD simulations of isothermal ($T_{def} = 100$ K) uniaxial stepped simple tensile tests on bulk glassy PE, geometry, energy and stress based arguments are used to show that non-polymeric structural rearrangements are responsible for the general plastic deformation patterns at low and intermediate strains in linear amorphous polymers. As stated by Argon et al. [1,2] in the analysis of plastic deformations of amorphous materials, these stress-induced short-scale defects, termed shear transformation zones (STZ), are carriers of plastic deformation in amorphous materials regardless of their chemical structure [13]. For macro-molecular bodies chain straightening processes come into play later on during the strain hardening regime.

The rest of this paper is organized as follows. The simulation model, the method for generating specimens and the loading processes are first described. Subsequently, characteristics of the uniaxial stress–strain curve and components of the total potential energy are highlighted for small and intermediate strain levels. The geometry of deformation is analyzed by computing distributions of the local core volume (V_c) and the local atomic volume (V_v). The number of bead-contacts and the self and intra-chain entanglements are quantified to describe the interaction between constituent chains. In section 4 a data reduction technique, the Empirical Orthogonal Functions (EOF) method [36], is used to describe the vibrational motion of polymer chains around their equilibrium positions at prescribed strains and to determine the energy contents in each eigenmode of the normalized displacement correlation matrix. Following ideas of [37] for the definition of the atomic level stress tensor, and of works in biochemistry regarding the analysis of conformational changes in proteins termed as *protein quakes* [38], an approximation of the local stress tensor is obtained for each bead (united atom) at every prescribed strain by using Hardy's method [39]. The time averaged values of two

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