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A molecular simulation study to the deformation Behaviors and the size effect of polyethylene during nanoindentation

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ABSTRACT

We present the results of the large-scale molecular mechanics (MM) simulation during the nanoindentation of polyethylene (PE). The PCFF force field was taken to describe the interaction in the indenter-substrate system. A monocrystalline silicon indenter in truncated conical shape was driven to penetrate into PE substrate on which a molecular dynamics equilibrium has been performed. To accurately compute the projected contact area used in calculation of hardness, we measured the contact depth via judging the initial contact point. A reasonable load-displacement curve based on the contact depth was depicted. As for the serrated shape of load-displacement curve, we supposed that the alternant occurrence of elastic and plastic deformation in the substrate during the indentation process is the main reason. We verified this supposition by discussing the loading and several unloading curves. Based on the obtained load-displacement curve, we established a model to compute the hardness. The model presents obvious size effect that the hardness initially increases with the increase of contact depth till it reaches a hardness peak and then gradually decreases with further increase in contact depth. We explained the increase of hardness at the initial loading stage. The results reveal that size effect is the intrinsic characteristic of PE during nanoindentation since the model was s deviation which could also cause size effect.

1. Introduction

Nanoindentation has become one of the most commonly applied methods for determining modulus and hardness of polymer films at the micro- and nano-scales. However, similar to metals, the hardness and elastic modulus will increase with the decrease of the maximum indentation depth, which is called size effect [1,2]. Nanoindentation can be applied for the examination of the size effects at essentially all micromechanically relevant length scales [3]. Hardness model is also often applied for describing the size effect law. Modeling the hardness models and explaining the indentation size effects in polymers are of great importance since polymers are widely used in advanced technology [4–6].

Indentation size effects in polymers have been experimentally observed and analyzed. Based on molecular yielding theory [7], Lam et al. [2] developed a strain gradient plasticity model for plastic size effects of glassy polymers. However, size effects have also been observed in elastic deformation of polymers [8–10]. As for elastic size effects, hardness models based on strain gradient elasticity theory have been developed by various authors [8,11–13]. For elasto-plastic materials, Han et al. [14] deduced a hardness model by including a Frank energy related indentation work term to the total indentation work. Although this model agrees well with experimental data by Briscoe et al. [15], it could not accurately calculate the hardness of polymers since many experimental factors could cause measurement deviation.

In nanoindentation experiment, the hardness can be commonly calculated using the formula proposed by Oliver and Pharr [16]: $H = \frac{P_{max}}{A_p}$, where P_{max} is the maximum load measured during one cycle of loading and unloading, and A_p, the projected contact area of the indenter, is the dependent variable of the contact depth h_c along which contact is made between the indenter and the substrate. In their method, the distinctly curved unloading curve was approximated to a power law relation firstly, then the slope of the upper portion of the unloading curve during the initial stages of unloading was defined as the contact stiffness S. The contact depth h_c is given by: $h_c = h_{max} - -\epsilon\frac{P_{max}}{S}$, then the projected contact area A_p is given by a area function: $A_p = A(h_c)$ which is approximated to describe the cross sectional area of a number of different shaped indenters. According to the O-P method, the accuracy of hardness measurement depends inherently on how well the maximum load P_{max} and the contact depth h_c are measured and how accurate the area function $A(h_c)$ is chosen. In experiment, several factors such as

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(1) the limitations of experimental resolution [17], (2) friction [18,19] and surface effect of the specimen [20], (3) the accuracy of numerical fitting of unloading curve [17], (4) tip defect of the indenter can cause measurement deviation. These factors can be negligible when the experiment is performed at the micrometer scale, but they could cause tremendous inaccuracy at a few nanometers scale.

Since the experiments could cause inaccuracy, the obtained hardness models by experiments are not able to accurately describe the size effect laws. What deserves more investigation is whether the experimental deviation itself causes the size effect or not. In other words, whether the size effect is an intrinsic characteristic of polymer or not. Based on these problems, a more reasonable method which doesn't include experimental deviation should be established. The deformation details of the polymer substrate during the indentation process should also be studied. To eliminate the experimental deviation, MM simulation is used in this paper since it is extremely convenient to observe the details during indentation. Recently, many related works have been reported. Zeng et al. [21] studied the reinforcing mechanism of polyhedral oligomeric silsesquioxane (POSS) to polystyrene (PS) by nanoindentation simulation and proposed a method to compute the hardness of the simulated materials. Hu [22] revealed the reinforcing impact of POSS to polyethylene (PE) under different shapes of diamond indenters. In the further work, Hu [23] found that the slipping between molecular chains is the main source of the loading drop during nanoindentation.

In the present work, we performed the MM simulation of polyethylene (PE) during nanoindentation. Firstly we built an amorphous cell of PE as the substrate and a monocrystalline silicon indenter in truncated conical shape. Then the indentation process was simulated with PCFF force field [24–28]. After an NVE dynamic equilibration was performed on the substrate, the indenter was driven at a certain distance toward the substrate at each step. The results and discussions section is organized as follows. Firstly we clarified the initial contact point where the indenter tip essentially contacts the substrate. We defined the indentation depth starting from the initial contact point as the contact depth. These work is very important for calculation of hardness and also is the core purpose of this study. Based on the contact depth, we depicted a load-displacement curve. The obtained curve presents the serrated shape in the whole stage. Secondly we analyzed the alternant occurrence of elastic and plastic deformation details of substrate via discussing the unloading curve back from several contact depths. We verified that the alternant elasto-plastic deformation of substrate cause the serrated shape of the curve. Finally we established a hardness calculation model of PE via fitting the serrated load-displacement curve. The model presents obvious size effect that the hardness initially increases and finally decreases with the contact depth. We analyzed the reason of the increase of hardness at initial stage. We give the conclusions of this work in Section 4.

2. Simulation methodology

2.1. Simulation models

A nanoindentation simulation system consists of a substrate and an indenter. In order to built the substrate, a single PE molecular chain with a polymerization degree of 100 (shown in Fig. 1(a)) was generated firstly. Then 400 chains (240,800 atoms) were packed into a cubic cell to form an amorphous PE cell at a density of 0.98 g/cm^3 using the Amorphous Cell module in Materials Studio software packages from Accelrys Inc. The confined layer function in the software was chosen to obtain a smooth upper surface. The size of the cubic cell is 132.6183 Å × 132.6183 Å × 176.6510 Å. The amorphous PE cell is shown in Fig. 1(b). It should be mentioned that the obtained amorphous PE cell here isn't natural and reasonable since many molecular chains display straight line shape and the distribution of different types of atoms is uneven. To get a more reasonable configuration, a dynamic equilibration was performed later. The initial PE configuration data was imported to LAMMPS [29], and then the size of the cell was extended to 132.6183 Å × 132.6183 Å × 326.6510 Å with all atoms kept in the original positions.

In the extended space above the substrate, we built a monocrystalline silicon indenter which has a lattice parameter of 5.43 Å and the same lattice structure as diamond indenter commonly used in nanoindentation instrument. As shown in Fig. 2, the conical indenter was selected in accordance with the Berkovic indenter commonly used in experiment. Considering the tip defect effects, the indenter tip was truncated. The indenter consists of 7044 atoms, and the radii of both ends of the indenter are set as 5.0 Å and 50.0 Å respectively, and the height is 50.0 Å. The axis of the indenter is parallel to z axis and passes through the center of x-y plane. The original distance between the tip and the substrate upper surface was ~55.0 Å. The simulation system is shown in Fig. 3(a). The indenter was built in LAMMPS and all computation in the present work was performed in LAMMPS.

The PCFF force field is employed to describe the interactions between atoms. In PCFF force field, the total energy is divided into valence energies, cross energies and nonbonded energies. According to the built system, only nonbonded interactions exist between indenter atoms (Si) and substrate atoms (C and H) since there are no valence bonds. The nonbonded van der Waals interactions E_{VDW} between atom i and atom j is expressed by the following equation [24,26,27]:

$$E_{\mathrm{VDW}} = \varepsilon_{ij}^{0}\left[2\left(\frac{r_{ij}^{0}}{r_{ij}}\right)^{9} - 3\left(\frac{r_{ij}^{0}}{r_{ij}}\right)^{6}\right] \quad (r < r_c) \tag{1}$$

where r_c is the cutoff distance, which is set as 12.5 Å for all atoms in our work. r_{ij} and r_{ij}^{0} are the instantaneous and equilibrium distance between atom i and atom j, respectively. ε_{ij}^{0} is the coefficient of well-depth energy. r_{ij}^{0} and ε_{ij}^{0} can be obtained by the following equations [30,31]:

$$r_{ij}^{0} = \left(\frac{(r_i^0)^6 + (r_j^0)^6}{2}\right)^{\frac{1}{6}} \tag{2}$$

$$\varepsilon_{ij}^{0} = 2\sqrt{\varepsilon_i^0 \cdot \varepsilon_j^0}\left(\frac{(r_i^0)^3 \cdot (r_j^0)^3}{(r_i^0)^6 + (r_j^0)^6}\right) \tag{3}$$

The parameters r_i^0 and ε_i^0 used in our work are shown in Table 1 [30,31].

2.2. Simulation details

After the simulation system was built, the simulation was performed. The simulation comprises the equilibrium and indentation stages, and they were both carried out under periodic boundary conditions in all sides. Although the periodic boundary condition was set in z direction, the extended space in z direction was large enough to simulate the free boundary in accordance with the experiment. The bottom atoms as thick as 10 Å were constrained as fixed to simulate the fixed boundary in −z direction. During the equilibrium stage, the indenter tip and the substrate surface were positioned ~55 Å apart from each other so that there nearly were no interactions between the indenter and the substrate. Then