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ScienceDirect
Acta Materialia 57 (2009) 3615–3622
Acta MATERIALIA
www.elsevier.com/locate/actamat

Probabilistic molecular dynamics evaluation of the stress–strain behavior of polyethylene

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Received 8 August 2008; received in revised form 15 March 2009; accepted 15 April 2009
Available online 18 May 2009

Abstract

The primary goal of this study was to utilize molecular dynamics to predict the mechanical behavior of polyethylene. In particular, stress–strain relationships, the Young's modulus and Poisson ratio were predicted for low-density polyethylene at several molecular weights and polymer configurations with the number of united CH_2 atoms ranging between 500 and 5000. Probabilistic Monte Carlo methods were also used to identify the extent of uncertainty in mechanical property predictions. In general, asymptotic behavior was observed for stress and the Young's modulus as the molecular weight of the models increased. At the same time, significant variability, of the order of 1000% of the mean, in the stress–strain relationships and the Young's modulus predictions was observed, especially for low molecular weight models. The variability in the Young's modulus predictions ranged from 17.9 to 3.2 GPa for the models ranging from 100 to 5000 CH_2 atom models. However, it was also found that the mean value of the Young's modulus approached a physically possible value of 194 MPa for the 5000 atom model. Poisson ratio predictions also resulted in significant variability, from 200% to 425% of the mean, and ranged from 0.75 to 1.30. The mean value of the Poisson ratios calculated in this study ranged from 0.32 to 0.44 for the 100 to 5000 atom models, respectively.

Keywords: Molecular dynamics simulations; Mechanical properties; Amorphous polymers; Probabilistic modeling

1. Introduction

Nanomaterials usually exhibit significantly different physical and chemical behavior than macroscale material [1]. Therefore, the accurate characterization of nanomaterials is important in the advancement of nanotechnology and its applications. Multiscale modeling techniques have been identified as a relatively inexpensive computational tool that can be utilized to predict nanomaterial behavior. The accurate prediction of both physical and chemical properties from the nanoscale to the macroscale while not losing appropriate structural behavior has been acknowledged as a challenge in the application of multiscale modeling of materials [2]. As such, molecular dynamics (MD) simulations, one of several multiscale modeling techniques, can be used to predict nanoproperties of materials including various types of polymers.

MD simulation uses potential field interactions of atoms and molecules in order to predict mechanical, electrical and chemical behavior of a material through the solution of the equations of motion. Recently, MD simulations have been utilized in the prediction of material behavior for a number of polymers (e.g. polyethylene, polycarbonate, polyimide), polymer-based composites and nanocomposite materials (e.g. bucky-ball composites, nanotube composites). This includes the work done by Adnan et al. [3], Brown and Clarke [4], Frankland et al. [5], Fukui et al. [6], Odegard et al. [7], Simoes et al. [8], Theodorou and Suter [9], Valavala et al. [10], Valavala and Odegard [11], Yashiro et al. [12] and Zhu et al. [13]. However, most of these studies have evaluated only a small number of initial polymer configurations. Most studies considered 2–5 initial configurations, with the most (nine initial configurations) being evaluated

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doi:10.1016/j.actamat.2009.04.023

by Adnan et al. [3]. Probabilistic modeling techniques, which introduce an increase in the number of initial polymer configurations, have yet to be implemented in combination with MD procedures. Traditionally, probabilistic analysis uses inputs defined as distributions of values in order to predict a distribution of performance or outcome, instead of deterministic evaluations [14]. As the creation of the initial configurations in molecular dynamics involves random placement of molecules, a probabilistic approach could be used to evaluate the potential effects on material property predictions.

Thus, the objective of this study was to incorporate probabilistic analysis techniques to identify the variability in mechanical property predictions of polymers calculated using MD simulations and to evaluate the influence of molecular weight and the number of polymer molecules on the predictions. Low-density polyethylene (PE) was taken as a model polymer.

2. Methods

2.1. Molecular model

Simple PE was modeled due to its broad range of applications [15–17] and as a building block for more complex polymer-based structures. A PE density of 0.80 g cm^{-3} was used in order to compare with the appropriate literature [3,5,7]. High-density PE models were also developed and analyzed, and the corresponding results can be found elsewhere [18].

All MD simulations were performed using the Tinker software package [19] with a time step of 1 fs and a temperature of 300 K. Here, the time step implemented was similar to that in the literature which ranged from 0.5 fs [3] to 2.5 fs [4]. Tinker uses a velocity Verlet integration method to solve the equations of motion presented in MD [20,21]. Following Verlet's approach, a particle's trajectory is determined by the sum of forces acting on a particle as well as previous particle positions. The Verlet approach is utilized in Tinker's DYNAMIC subroutine. Tinker provides temperature and pressure constraints via the Groningen method of coupling to external baths [22].

A modified potential field was applied to account for the use of CH_2 united atoms within the molecular models instead of an explicit, all-inclusive, carbon and hydrogen atom model. United atom (UA) models have been used extensively in the literature [3–5,12,23] and have been shown to be more computationally efficient than explicit atom models due to the reduction in the number of potential field interactions with negligible effects on material property estimates [24,25]. The molecular system was modeled using bond stretching, bending, torsion and non-bonded interaction parameters for CH_2 united atoms (see Table 1), available in the literature [26,27].

Initially, a single PE molecule was modeled at several different molecular weights without consideration of multiple molecule effects according to Table 2. Consideration of multiple molecule effects was only introduced in two of the molecular weight models, those containing 2500 atoms and 5000 atoms. Thus both the effect of molecular weight and of multiple chains were evaluated in this research.

Periodic boundary conditions have been used extensively in the literature (e.g. [28]). In this work cubic periodic boundary conditions were imposed on the system, with an edge length according to Table 2 for the different models. The periodic dimensions were prescribed to achieve a density of approximately 0.80 g cm^{-3}. The size of the models and the appropriate number of atoms can be seen in Fig. 1.

2.2. Pre-strain equilibrium

Each PE molecular configuration was created using a random walk technique as a freely jointed molecule [29]. After the model geometry was generated and periodic

Table 2
Number of atoms and corresponding parameters used for large system analysis as well as multiple molecule models.

No. of atoms	Molecular weight (g mol^{-1})	Density (g cm^{-3})	Periodic dimension (nm)
5000	70,135	0.8	5.247
2500	35,068	0.8	4.1645
1250	17,534	0.8	3.3054
500	7014	0.8	2.424
100	1403	0.8	1.4242
	No. of atoms	No. of molecules	No. of total atoms per molecule
	2500	10	250
	2500	5	500
	2500	2	1250
	2500	1	2500
	5000	10	500
	5000	1	5000

Table 1
Governing equations for PE force field, potential parameters at 300 K where r_0 is the equilibrium bond length, θ_0 is the equilibrium bond angle, m is a phase change constant, and σ is the equilibrium non-bonded length; k_r, k_θ, k_ϕ and ε are all energy parameters [26,27].

Interaction type	Potential equation type	Governing equation	Force field constants
Bonded	Harmonic	$U(r_b) = k_r \sum (r_i - r_o)^2$	$r_0 = 0.153$ nm, $k_r = 26000$ kcal mol^{-1} nm^{-2}
Bond angle	Harmonic	$U(\theta) = k_\theta \sum (\theta_i - \theta_0)^2$	$\theta_0 = 1.91$ rad (109.5°), $k_\theta = 63$ kcal mol^{-1} rad^{-2}
Torsion	Cosine	$U(\phi) = k_\phi[1 + \cos(m\phi)]$	$m = 3.0$, $k_\phi = 1.0$ kcal mol^{-1}
Non-bonded	Lennard–Jones	$U(r_b) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$	$\varepsilon = 0.113$ kcal mol^{-1}, $\sigma = 0.428$ nm, $rx_{cut} = 1.07$ nm