



Stochastic predictions of bulk properties of amorphous polyethylene based on molecular dynamics simulations

N. Vu-Bac^{a,b}, T. Lahmer^{b,c}, H. Keitel^c, J. Zhao^b, X. Zhuang^{a,*}, T. Rabczuk^{b,c,d,*}

^a Department of Geotechnical Engineering, Tongji University, Shanghai 200092, China

^b Institute of Structural Mechanics, Bauhaus-Universität Weimar, Marienstr. 15, D-99423 Weimar, Germany

^c Graduiertenkolleg 1462, Bauhaus-Universität Weimar, Germany

^d School of Civil, Environmental and Architectural Engineering, Korea University, South Korea

ARTICLE INFO

Article history:

Received 9 January 2013

Received in revised form 19 June 2013

Available online 24 August 2013

Keywords:

Sensitivity analysis

Molecular dynamics (MD)

Polyethylene-like polymer (PE)

Response surface method

Variance-based methods

Elementary effects

ABSTRACT

The effect of the chain length, the temperature and the strain rate on the yield stress and the elastic modulus of glassy polyethylene is systematically studied using united-atom molecular dynamics (MD) simulations. Based on our MD results, a sensitivity analysis (SA) is carried out in order to quantify the influence of the uncertain input parameters on the predicted yield stress and elastic modulus. The SA is based on response surface (RS) models (polynomial regression and moving least squares). We use partial derivatives (local SA) and variance-based methods (global SA) where we compute first-order and total sensitivity indices. In addition, we use the elementary effects method on the mechanical model. All stochastic methods predict that the key parameter influencing the yield stress and elastic modulus is the temperature, followed by the strain rate.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Glassy amorphous polyethylene (PE) has been widely studied by many researchers due to its important physical, chemical and mechanical properties. Great effort has been made for many decades to predict the mechanical properties such as Young's modulus, yield strength, etc. Recent developments of molecular dynamics simulation have opened the door for understanding and predicting the mechanical and physical properties of various polymeric materials. Capaldi et al. (2002) noticed that the elastic modulus and yield stress depends on the rate of deformation. Recently, Zhao et al. (2010) have found that the chain length, temperature and strain rate have a significant effect on the mechanical properties of amorphous PE under uniaxial deformation. The thermo-mechanical properties

of PE were studied by coarse-grained MD simulations. Boyce and Arruda (2000) stated when more than 100 atoms (units) are used in a chain, the chain will take on a randomly kinked shape and the polymer chains are arranged in a random orientation. Hossain et al. (2010) showed the higher the chain length, the more entanglement the structure and hence the structure has a higher stiffness and yield stress. They also reported that the influence of the chain length on the stress–strain curve is more significant than the number of chains. Robert and Mark (2006) observed strain softening for specific chain lengths. The influence of certain parameters on the mechanical behavior of glassy amorphous polymers has been obtained qualitatively (Hossain et al., 2010; Robert and Mark, 2006; Capaldi et al., 2004). However, quantitative results in the context of stochastic analysis are missing.

This paper is the first attempt to quantify the influence of the chain length, temperature and strain rate on the yield stress and elastic modulus. Therefore, we compute first-order, total-effect sensitivity indices in the context of global sensitivity analysis (SA). Moreover, we perform

* Corresponding authors at: Department of Geotechnical Engineering, Tongji University, Shanghai 200092, China

E-mail addresses: xiaoyingzhuang@tongji.edu.cn (X. Zhuang), timon-rabczuk@uni-weimar.de (T. Rabczuk).

a local SA where we calculate partial derivatives and elementary effects.

The paper is outlined as follows. In Section 2, we briefly describe the MD model for PE. The results of the MD model will be shown in Section 3. Section 4 describes the SA. In Section 5, the coefficients of determination and the sensitivity indices will be presented before we discuss the numerical results. Finally, we end the manuscript with concluding remarks and future work.

2. Molecular dynamics method

A united atom approximation is utilized in which the methyl groups are represented by a single “atom” or unit. The effect of the hydrogen atoms on the polymer configuration is accounted for in the present potentials, while the mass is included in the united atom. Atomic charges and electrostatic interactions are not considered here (Zhao et al., 2010; Zhang et al., 2012). The functional form and parameters of the force field (Hossain et al., 2010) are summarized in Table 1.

The initial chain structures were created by implementing a Monte Carlo random walk growth algorithm with rigid bond length (Binder, 1995). The simulation cell had a face centered cubic (FCC) lattice each site representing a possible monomer location. Similar methods have successfully been generated in Hossain et al. (2010) and Shepherd (2006).

According to Hossain et al. (2010) and Bouvard et al. (2006), each generated structure (10,000 atoms) is equilibrated for 100 ps ($\Delta t = 1.0$ fs) so that the volume and energy of the system becomes stable, keeping both the temperature $T = 500$ K and the volume in the NVT ensemble controlled by the Nose–Hoover’s thermostat (Nose, 1984; Hoover, 1985). Then, the system is kept at a temperature of $T = 500$ K and pressure $P = 0$ atm for 500 ps ($\Delta t = 0.5$ fs) in the NPT ensemble. After the process, the system is cooled down to the given temperature with a cooling rate of 0.8 K/ps by the same NPT process followed by further 500 ps NPT ensemble at the desired temperature. These structures are generated after the equilibration process in a cubic space in order to accurately calculate the mechanical properties. After the equilibration process, uniaxial tension tests are performed to obtain the stress–strain response in dependence of different chain lengths, temperatures and strain rates in the NPT ensemble. Fig. 1 illustrates the undeformed (left) and deformed (right) representative volume elements.

To verify the glass transition temperature of various thermodynamics quantities, two consecutive equilibration

steps were implemented (Hossain et al., 2010). Firstly, the model (20,000 atoms) was equilibrated at 500 K. Then, the system was cooled down to 100 K at a rate of 0.8 K/ps over 500 ps by a series of NPT runs. The glass transition temperature was identified as the location of the discontinuity in the slope of the specific volume versus temperature curve are shown in Fig. 2.

3. Molecular dynamics simulation results

In this section, the influence of the chain length, temperature and strain rate on the mechanical properties of PE is obtained by UA-MD simulations.

Gaussian, Schulz–Flory, log normal and the Poisson distribution are often used (David, 2001) to approximate the chain length distribution. A small number of monomers (N_e) does not increase the strength because short chains slip too easily (<http://mmrl.ucsd.edu/>). The strength increases with the chain length (N_e), but so does viscosity (hard to mold) if N_e is larger than 2000 units. The experimental studies of Ungar et al. (1985) and Lee and Wegner (1985) on the linear long-chain showed that polymer chains kink only for chain lengths larger than 100 CH_2 units, the so-called entanglement length (Sundararajan and Kavassalis, 1995). In our simulations, 100 to 2000 units are chosen as lower and upper bounds of a truncated Gaussian distribution.

For glassy PE, the temperature should be lower than the glass transition temperature T_g ($T_g = 300$ K, see Fig. 2). However, the temperature has to be high enough to observe strain-rate effects for the thermal equilibrium (Capaldi et al., 2004). Brown and Clarke (1991) pointed out that the Young’s modulus decreases significantly when the temperature increases above 100 K. Therefore, we modify the temperature from 100 K to 300 K assuming uniform distribution. Fig. 3 shows a typical stress–strain curve.

The elastic modulus and the yield stress decrease with decreasing strain rate. As only a few pico- or nano seconds can be modeled in MD simulations, strain rates below 10^9 1/s cannot be captured though they are unrealistic in practical applications. Constant true strain rates ranging from 5×10^9 to 5×10^{10} 1/s are used in our MD simulations (Capaldi et al., 2004). We assume a uniform distribution.

The stress–strain response for glassy amorphous PE system with 10 chains, 1000-units deformed in uniaxial tension at temperature of 250 K and strain rate of 1×10^{-5} 1/fs is shown in Fig. 3. Stress–strain curves with

Table 1
Functional form and parameters of the force field of united atom polyethylene.

Interaction	Form	Parameters
Bond	$E_{bond} = \frac{1}{2} k_b (l - l_{eq})^2$	$k_b = 350$ kcal/mol \AA^2 , $l_{eq} = 1.53$ \AA^2
Angle	$E_{angle} = \frac{1}{2} k_\theta (\cos(\theta) - \cos(\theta_{eq}))^2$	$k_\theta = 60$ kcal/mol/rad 2 , $\theta_{eq} = 109.5^\circ$
Torsional	$E_{torsional} = \frac{1}{2} \sum_{i=0}^3 k_n \cos^n(\phi)$	$k_0 = 1.736$, $k_1 = -4.490$, $k_2 = 0.776$, $k_3 = 6.990$ (kcal/mol)
Non-bonded	$E_{non-bond} = \begin{cases} 4\epsilon(\frac{r_c}{r})^{12} - (\frac{\sigma}{r})^6 & r < r_c \\ 0 & r \geq r_c \end{cases}$	$\epsilon = 0.112$ kcal/mol, $\sigma = 4.01$ \AA , $r_c = 10.5$ \AA

Download English Version:

<https://daneshyari.com/en/article/802809>

Download Persian Version:

<https://daneshyari.com/article/802809>

[Daneshyari.com](https://daneshyari.com)