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Research Paper

An atomic finite element model for biodegradable polymers. Part 1. Formulation of the finite elements

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ABSTRACT

Molecular dynamics (MD) simulations are widely used to analyse materials at the atomic scale. However, MD has high computational demands, which may inhibit its use for simulations of structures involving large numbers of atoms such as amorphous polymer structures. An atomic-scale finite element method (AFEM) is presented in this study with significantly lower computational demands than MD. Due to the reduced computational demands, AFEM is suitable for the analysis of Young's modulus of amorphous polymer structures. This is of particular interest when studying the degradation of bioresorbable polymers, which is the topic of an accompanying paper. AFEM is derived from the interatomic potential energy functions of an MD force field. The nonlinear MD functions were adapted to enable static linear analysis. Finite element formulations were derived to represent interatomic potential energy functions between two, three and four atoms. Validation of the AFEM was conducted through its application to atomic structures for crystalline and amorphous poly(lactide).

1. Introduction

Biodegradable polymers such as poly(lactide), poly(glycolide) and poly(caprolactone) have been used in medical applications for several decades. However, their mechanical properties are not fully understood due to the complex nature of both polymer theory and degradation. Recent studies modelling mechanical property degradation have begun to increase knowledge in the area (Ding et al., 2011; Wang et al., 2010). Further insights into biodegradable polymer properties and degradation mechanisms may be achieved through atomic analysis. This opportunity has generated interest in the development of molecular dynamics (MD) force fields for poly(lactide) (Blomqvist et al., 1999, 2000; McAliley, 2009; McAliley and Bruce, 2011). These force fields

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describe the interactions between atoms by relating the atomic coordinates to interatomic potential energy.

Ding et al. (2011) studied the chain scission of a polyethylene atomic structure through MD simulations. It was not possible for Ding et al. (2011) to use a complex molecular structure, such as poly(lactide), due to the high computational requirements of MD simulations. This limitation has led to research into more computationally efficient simulation methods. The procedure used in MD simulations is as follows: (i) calculate the instantaneous forces applied by the atoms to one another; (ii) calculate the atomic acceleration that results from the forces; (iii) calculate the speed and distance travelled by each atom in a discrete time period; (iv) calculate the new atom positions and repeat from step (i). This computationally intense process can be simplified by using molecular statics, in which the simulation can be considered to include a damping force that gradually removes energy from the system until the atoms have zero velocity. Although molecular statics simulations require less computational power than molecular dynamics, amorphous polymers still present a computational challenge. Especially when repeated simulations are required, for example when analysing a polymer during degradation.

To enable the analysis of more complex structures, or to enable a greater number of simulations, several authors have developed more computationally efficient method for atomic analysis (Liu et al., 2004, 2005; Wang et al., 2003, 2006). Liu et al. (2004, 2005) developed an atomic-scale finite element method (AFEM) in which the molecular dynamics force field is represented by finite elements. Their method offered significant reductions in computational demands versus the conjugate gradient method in molecular mechanics. For nonlinear potential energy functions, an iterative procedure was required in order to minimise the total potential energy in a structure. Wang et al. (2003, 2006) also developed atomistic finite elements to represent the interaction between atoms through finite element analysis. The elements they developed represent the polymer as a chain of elastic rods connected to each other by elastic joints, which facilitate angular potential energy terms to be considered. Again, an iterative procedure was used in the simulations. The work of Liu et al. (2004, 2005) and Wang et al. (2003, 2006) demonstrate the value of atomistic finite element methods. However, due to the iterative nature of their methods, the computation benefits over MD are limited.

This study presents a new atomic finite element method (AFEM), in which nonlinear interatomic potential energy functions are adapted to enable static linear analysis. Simulations are completed in a single step as opposed to numerous iterations. The reduced computational demands permit the analysis of large atomic structures, including amorphous poly(lactide). This simplification is possible if one is only interested in very small displacement of atoms from their equilibrium positions, such as when calculating Young's modulus of a polymer. Atomic finite elements are specifically formulated to represent all atomic interactions in the PLAFF2 (McAliley, 2009) molecular dynamics force field for poly(lactide). In this first paper of a two-part series, the AFEM simulation technique is developed and demonstrated for crystalline and amorphous poly(lactide) structures. In the second paper (Gleadall et al., in press) the effect of polymer chain scission on the degradation of Young's modulus is analysed. Such analysis has not previously been conducted for an atomic model of a biodegradable polymer. The AFEM simulation results are used to develop a numerical model for Young's modulus change of degrading polymers.

2. Molecular dynamics polymer force field

In molecular dynamics, the interactions between atoms are described by force fields that relate atomic coordinates to potential energy. McAliley (2009) developed the PLAFF2 force field specifically for poly(lactide) and supplied it as supplementary information with his thesis. This force field is used as a basis for the AFEM approach presented in this study. This section gives a brief overview in Eqs. (1)–(8) of the atomic interactions described by the force field. Further details can be found in McAliley's thesis (McAliley, 2009) and in the manual of the MD software Gromacs (van der Spoel et al., 2010). Fig. 1 shows a four-atom section of a polymer chain. Several different forms of atomic interaction are shown. In the force field, each type of interaction is represented by a potential energy function. Potential energy is calculated for covalently bonded atoms based on:

- interatomic separation (the bond-stretch potential energy);
- the angle between adjacent bonds (the bond-angle potential energy);
- and rotation of the polymer chain about a bond (the bond-dihedral potential energy).

The figure also shows how potential energy is associated with the interatomic separation of atoms that are not covalently bonded (the nonbond potential energy). These potential energy forms combine to represent the overall atomic interaction in a material. Although the AFEM approach presented in this study is based on a specific force field, it simply translates to a wide range of force fields for different materials.

Atomic simulations of material properties typically consider the potential energy of a representative unit cell of polymer, which repeats to infinity in all directions. The total potential energy of the unit cell, V_{MD} (kJ mol^{-1}), according to the PLAFF2 force field is given in Eq. (1) as

$$V_{MD} = \sum_{\substack{\text{bonds}\\ i,j}} V_b + \sum_{\substack{\text{angles}\\ i,j,k}} V_a + \sum_{\substack{\text{dihedrals}\\ i,j,k,l}} V_d + \sum_{\substack{\text{nonbonds}\\ i,j}} V_{nb} - Fu \quad (1)$$

which is the sum of potential energies for all bond-stretch, V_b, bond-angle, V_a, bond-dihedral, V_d, and nonbonded, V_{nb} (all kJ mol^{-1}), atomic interactions. The term Fu is the applied work due to an externally applied force, F (N), and the displacement where F is applied, u (nm). In molecular statics simulations, the atomic coordinates are found such that V_{MD} is minimised. The minimisation of potential energy results in the atomic configuration that the force field suggests is likely to exist in a real material. When an overall force is applied to the material and results in a strained atomic configuration,