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Predicting the mechanical behavior of amorphous polymeric materials under strain through multi-scale simulation

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ABSTRACT

Polymeric materials have become the reference material for high reliability and performance applications. However, their performance in service conditions is difficult to predict, due in large part to their inherent complex morphology, which leads to non-linear and anisotropic behavior, highly dependent on the thermomechanical environment under which it is processed.

In this work, a multiscale approach is proposed to investigate the mechanical properties of polymeric-based material under strain. To achieve a better understanding of phenomena occurring at the smaller scales, the coupling of a finite element method (FEM) and molecular dynamics (MD) modeling, in an iterative procedure, was employed, enabling the prediction of the macroscopic constitutive response. As the mechanical response can be related to the local microstructure, which in turn depends on the nano-scale structure, this multiscale approach computes the stress–strain relationship at every analysis point of the macro-structure by detailed modeling of the underlying micro- and meso-scale deformation phenomena.

The proposed multiscale approach can enable prediction of properties at the macroscale while taking into consideration phenomena that occur at the mesoscale, thus offering an increased potential accuracy compared to traditional methods.

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1. Introduction

Polymers are complex macromolecules whose structures range from the angstrom level of a backbone bond within a single chain, to the scale of the radius of gyration, which can reach tens of nanometers. Polymeric morphological structures in melts, blends and solutions can range up to the millimeter scale and larger. The corresponding time scales of the dynamic processes span an even wider range, from sub-picoseconds for atomic vibrations, to seconds for crack propagation in composites, or even hours for phase separation in blends [1,2]. Amorphous polymers contain a complex network of molecular chains with random spatial arrangements that dictate the bulk mechanical properties [3]. Macroscopic (measurable) properties of polymers depend on the properties at

several smaller scales [4]; different length scales imply different levels of detail or resolution of the analysis [2].

The macroscopic properties of amorphous polymers are strongly influenced by many factors such as testing conditions (temperature and strain rate) [5], chain entanglements [6], and interphase dynamics and morphology when inclusions are added to the polymer matrix [7,8].

To characterize a polymer it is essential to understand the properties of a system across several length scales, from nanoscopic to macroscopic dimensions [9]. One way to study the properties and behavior of complex materials, such as polymers, is through computer modeling and simulation. Computer simulations can provide information not accessible experimentally, reducing expensive and time-consuming trial-and-error approaches, and are particularly effective in exploring the physical and mechanical properties of new materials [10].

One of the main goals of computational materials science is to increase the speed and accuracy of the prediction of properties and features of new materials, which cannot be achieved with

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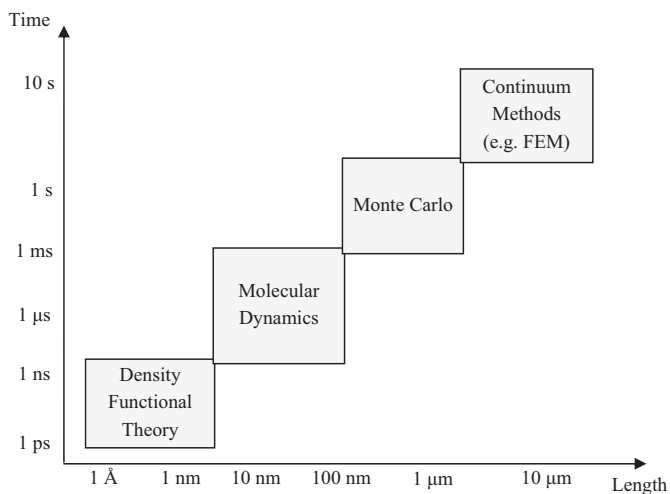*E-mail addresses:* rsimoes@ipca.pt, rsimoes@dep.uminho.pt (R. Simoes).

Time

Fig. 1. Length and time scales associated with computer simulations. Axes not to scale.
Adapted from [12].

traditional simulation methods at a single length and time scale. Since no single model is capable of covering the enormous length and time scales associated with polymeric materials, a multiscale method is required in order to accurately predict the macroscopic properties and behavior of materials from a detailed fundamental molecular description [1,2,11]. Fig. 1 shows the length and time scales associated with computer simulations.

In the present work, tensile tests were simulated for polycarbonate (PC), from which stress–strain curves were drawn and the Young modulus and Poisson ratio calculated. It has been pointed out that stress–strain behavior meaning can be lost as soon as localization starts [13]. Properties of the polymer matrix and its viscoelastic behavior were already studied in the past through molecular dynamics [14–16], as well as deformation mechanisms for both neat polymers and polymer-based composites [17].

The influence of temperature and strain rate on the mechanical properties, namely Young modulus, of PC and polymers in general has been investigated by different authors and it has been concluded that the Young modulus is strongly influenced by both factors [5,18], although tests for strain rates higher than $2000 \, s^{-1}$ are barely done [19]. In a PC uniaxial compressing test, Richeton et al. [5] stated that the Young modulus decreased with decreasing temperature at very low temperatures ($T \sim 200 \, K$), and exhibited a non-linear dependence on strain rate, at high strain rates. This latter effect was attributed to the decreasing molecular mobility as the strain rates increases. These same authors also developed a three-dimensional constitutive model to describe the mechanical response of amorphous polymers over a wide range of temperatures and strain rates. The simulated results were in good agreement with experimental observations [20]. The high dependency of the tensile behavior of PC on the strain rate, from tensile stress–strain responses at rates up to $1750 \, s^{-1}$, has been identified in several studies [21,22].

MD simulations and micromechanical modeling were used by Valavala et al. [23] to predict the bulk-level Young modulus of PC as a function of the representative volume element (RVE) size and two force fields: AMBER and OPSL-AA. Energy-biased micromechanics proved to be better in the calculation of the bulk modulus than microstate averages because the results were in better agreement with experiments. Microstate properties for each RVE were determined, and a wide range (0.09–20.9 GPa) of Young modulus values

was found. It was concluded that larger RVE sizes led to values closer to experimental results than smaller RVE [23].

The bulk elastic properties of PC were predicted in a study by Valavala et al. [3]. The molecular structure of several microstate cubic RVE of sides of the order of a few nanometers was the basis of the calculation. It was shown that individual microstates yield a wide range of predicted elastic properties but, when multiple microstates were considered, Young modulus predictions were closer to experimental results [3].

The main limitation of many of the multiscale methods proposed in the literature [24–30] is that they fix portions of the system treated at different scales and do not allow exchanges during the simulation [31].

Multiscale methods coupling molecular dynamics and extended finite element method [32] or coupling MD/coarse-grained-particle method [33] were presented for crack propagation. Baeurle [31] demonstrated the usefulness of field-theoretic approach as a valuable tool to solve multiscale problems involving the determination of physical properties of a wide variety of neutral and charged polymer materials, with the advantage of enabling the treatment of all levels of description [31]. Also, MD itself has already been used to study polymer tribology [34].

Saether et al. [35] proposed a new MD-FEM coupling based on a restatement of the standard boundary value problem for the definition of a coupled domain. Simulations have demonstrated the effectiveness of embedded statistical coupling method to couple atomistic and continuum modeling within a unified multiscale simulation [35].

Huang et al. [36] presented a molecular dynamics-continuum coupled model; and a multiscale MD-FEM method was developed by Mortazavi et al. [37] for evaluating thermal conductivity of nanocomposites.

The correlation between polymer microstructure and its anisotropic uniaxial stress when subjected to a uniaxial constant strain rate has been studied by Srivastava et al. [38]. Mean square bond length and mean bond angle influence the uniaxial stress. The density of the polymer significantly affects the uniaxial stress–strain behavior, with a large jump in the uniaxial stress levels as the density increases. Chain length also influences the characteristics of the material; while short chains behave like rigid molecules, long chains are very sensitive to the loading and external environment [38].

In the present paper, a bridge between the meso and macroscale is attempted by introducing information resulting from the first into the latter, namely Young's modulus and Poisson's ratio. Mesoscale analysis is carried out through Molecular Dynamics (MD) simulations, while the Finite Element Method (FEM) is applied at the macroscale.

2. Simulation model

2.1. Molecular dynamics

Molecular Dynamics (MD) is a computer technique which allows the prediction of the time evolution of a system of interacting particles. It is a deterministic method which can be used to solve molecular models encompassing thousands or even millions of atoms at the atomistic or molecular level [39,40].

First, a set of initial conditions is defined. These comprise the initial velocities and initial positions of all the particles in the system. Then, the potential energy that governs interactions between particles must be properly chosen. This choice is crucial in MD simulations since the interactions within and between polymer chains have a big influence on the macroscopic properties of the material.