

Mechanical Behavior and Structure-Properties Relationships in Amorphous Polymers Simulated by Molecular Dynamics

Ricardo Simões¹, Júlio C. Viana¹, Gustavo R. Dias¹, António M. Cunha¹

Summary

Polymeric systems comprised of coiled chains arranged in three-dimensional space have been simulated using the molecular dynamics method. The computer-generated materials are created by emulating the step-wise polymerization process, resulting in a set of self-avoiding chains with controlled degree of orientation along a preferential axis.

During the simulation, a uniaxial tensile force is applied to the edges of the material and its response is monitored along time. The true stress levels and several global structure indicators are determined during the simulation in order to establish structure-properties relationships. The present paper deals with the effects of chain orientation on the mechanical properties and behaviour of amorphous polymeric materials at the mesoscale. Results clearly show that the degree of orientation of the chains with respect to the direction of the applied external force is paramount in determining the response at high strain levels.

This research follows previous work on similar systems to study the crack formation and propagation phenomena, deformation mechanisms at the nanoscale, and the influence of the loading conditions on the material behaviour. These simulations have improved the fundamental understanding of the underlying phenomena, thus enabling the design of knowledge-based materials with improved properties.

Introduction

As the number of applications based on polymers and polymer-based materials continuously grows, understanding their properties and behavior has become a topic of substantial interest. Although this class of materials has been successfully used for the better half of the last century, this was done following trial-and-error approaches, with very limited comprehension of the critical phenomena governing the material behavior.

As the specifications of leading-edge technological applications become too demanding for commodity polymers and even traditional heterogeneous composites, the need for developing knowledge-based materials is higher than

¹ Institute of Polymers and Composites, Department of Polymer Engineering, University of Minho, 4800-058 Guimarães, Portugal; rsimoes@dep.uminho.pt; amcunha@dep.uminho.pt

ever before. However, current experimental capabilities for studying advanced polymer-based materials are still unable to provide answers to pertinent questions, particularly about phenomena taking place at the molecular level.

Computer simulations of materials can help answer some of those questions, thus complementing information provided by experimental testing. As eloquently argued by Fossey [1], computational modeling and simulation presents several advantages, such as the ability to study phenomena taking place at length scales varying from the macroscopic to quantum levels, phenomena that occur too fast to follow experimentally (nanoseconds to picoseconds), and any conceivable material structure, including under ideal or extreme conditions (irreproducible in a laboratory). Variables can also be studied independently of one another.

Naturally, simulations also present several limitations, of which the most pertinent are size and length scale restrictions dictated by hardware capabilities, and the necessity to validate the model (at least conceptually and in some well defined case studies) through experiments. This becomes an issue when studying phenomena that cannot be seen or measured through experimental means.

The present paper follows previous work on the mechanical properties and the crack formation and propagation phenomena in two-phase polymer liquid crystals [2-3], the effect of the loading conditions on the behavior of the material [4], and the tribological behavior of one- and two-phase amorphous polymers [5].

Simulation Model

The polymer structure is modeled through the use of the statistical segment concept, as espoused by Flory [6]. Thus, in the computer generated material, each segment corresponds to a statistical segment representing a small part of a polymeric chain. Interactions between the segments are defined by potentials as a function of the inter-segmental distance, as discussed in [2]. Different potentials can be employed to describe the behavior of flexible or rigid segments, as well as different chemical structures of the repeating units. Distinct potentials are also used to represent primary (intra-chain) and secondary (inter-chain) interactions.

The present simulations were focused on amorphous polymeric structures of flexible segments. Thus, only two different potentials have been employed: a relatively broad spliced double-well potential for the intra-chain interactions and a much weaker Morse-like potential for the inter-chain interactions. The inter-chain interactions have a smoothed cut-off radius of 2.5σ (with σ being the equilibrium inter-segmental distance).

Simulations were performed using the molecular dynamics (MD) method, initially developed by Alder and Wainwright [7]. In the MD method, the segments are placed on a three-dimensional space, each segment being

characterized by its position and momentum. These values are recalculated for every particle in the system at every time step and can be continuously recorded.

At the start of the simulation, an external uniaxial tensile force is applied to both edges of the material along the x-axis, as shown schematically in Figure 1. The external force increases monotonously along time from the initial value of zero until the end of the simulation.

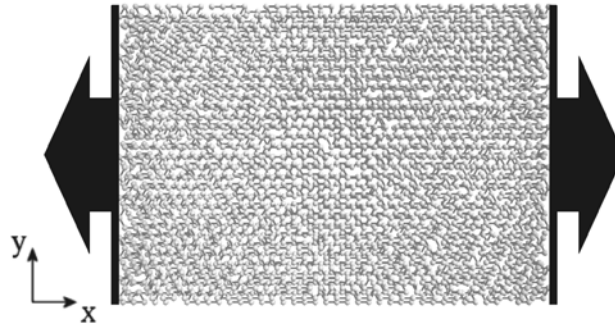


Figure 1 – Geometric arrangement of the coiled polymeric chain structure and the application of an external tensile force during simulation. The force is applied to the edge segments of the material along the x-axis.

Since fracture and failure are complex phenomena and difficult to describe mathematically, simulations are typically ran until one of several criteria is met. Depending on which phenomena is being studied and the parameters of interest, the user can subsequently review the simulation as a 3D animation and choose to pinpoint the actual moment of failure, defining it as the end of the run. In the present simulations, the termination criteria were: strain value of 2 along the x-axis, or 100 force steps (which are equivalent to 200 000 time steps). The value of the external tensile force is increased at each force step.

Material Generation

Creation of the polymeric computer-generated materials (CGMs) follows a procedure initially developed by Mom [8] and later adapted to result in more realistic polymer structures [9]. This procedure is similar to the step-wise polymerization process, with chains growing by bonding of neighboring segments. The resulting CGMs consist of self-avoiding coiled chains, and exhibit several realistic features, including a distribution of molecular weights, presence of defects, and chain entanglements.

The basic methodology followed to create the CGMs, including two-phase polymer liquid crystals (PLCs), has been detailed elsewhere [9] and will not be discussed here. However, it is important to describe a new feature of the material

generation code that allows controlled orientation of the material along a preferential axis. At the material generation stage, the direction of chain growth is controlled by a statistical function. Formation of bonds is allowed or denied by this function in order to result in an average orientation of the material as close as possible to that defined by the user. This feature constitutes the starting point for the work reported in the present paper. Naturally, the degree of orientation of the chains with the preferential axis will affect other quantities, such as the average chain length and the number of entanglements.

During the simulation, several variables are calculated at regular intervals to provide information about the status of material. Among these, the most important are strain, stress, average end-to-end distance of the chains, and chain orientation (using three different methods for determining orientation indicators).

Selected Results

Materials with varying degrees of preferential orientation with the x-axis were created following the procedure described in the previous section and in [9]. The orientation is expressed as the fraction of bonds aligned with the preferred direction (the x-axis in the present case). CGMs were created with orientations of 0.33 (no preferential direction), 0.50, 0.70, 0.80, 0.90, and 1.0 (complete alignment with the x-axis). Each CGM was subsequently simulated under the same loading conditions and model parameters.

Figure 2 shows the structure of the CGM with orientation of 0.50 at different stages of the simulation. Here, t is the force step at which the snapshot was taken.

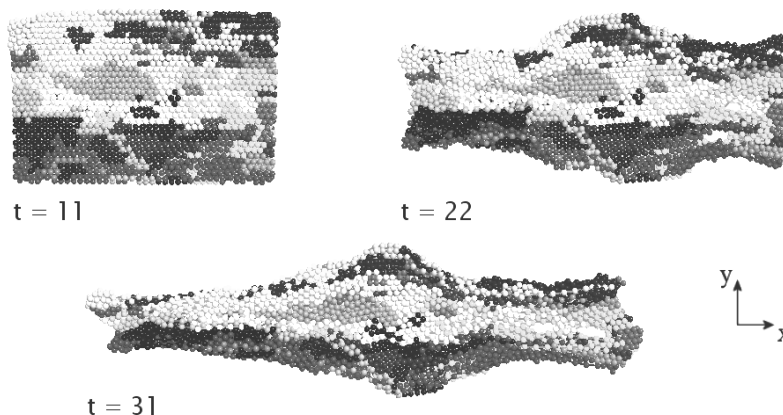


Figure 2 – Different stages during simulation of tensile deformation of a CGM with preferential orientation with the x-axis of 0.50. Each chain has been represented in a different shade of gray for ease of visualization.

As one can see in Figure 2, the structure suffers practically no changes during the first 10 force steps, as the applied external force is still small and thus insufficient to displace the segments from their positions. Whenever the force is high enough to overcome the secondary inter-chain interactions, plastic deformation begins. This process is not homogeneous, being dictated in each region in the material by the particular geometric arrangement of the chains at that location. Deformation extends from the edges to the center of the material, as the force has to be transmitted along the chains and the deformation mechanisms are more restricted in the inner regions.

The mechanical behavior of three of the studied materials is represented in Figure 3, in the form of stress vs strain curves. These clearly exhibit significantly different response at high strain levels under the same loading conditions. It is particularly interesting how the higher orientation causes a shift from predominantly ductile to predominantly brittle behavior.

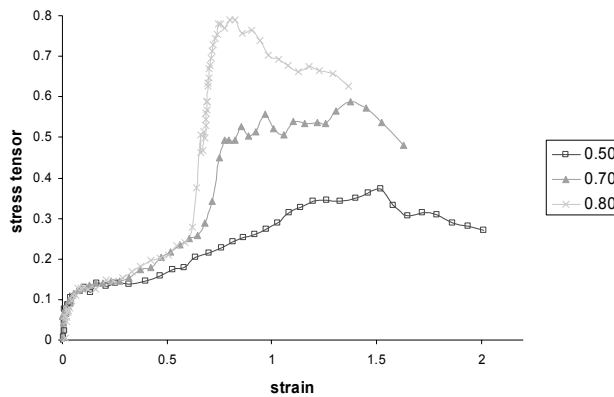


Figure 3 – Stress vs strain curves for materials with preferential orientation along the x-axis of 0.50, 0.70, and 0.80. For a description of the concept of stress tensor refer to [10].

One can also see from Figure 3 how the more oriented materials require higher values of applied force to cause fracture. Although the explanation for this behavior has to consider a variety of phenomena, it is mostly due to the fact that when the chains are more oriented with the force, significant deformation has to involve extension, conformation changes, or rupture of primary bonds (high energy processes), while in lower orientations, chain uncoiling and chain slippage (low energy processes) contribute significantly to deformation.

Although higher orientation increases material strength along the preferred axis, it simultaneously reduces the ductility, resulting in lower strain at break.

Concluding Remarks

The information resulting from these simulations provides a better understanding of the behavior of polymeric materials. A connection between the chain structure of the material and its mechanical properties has been established on the basis of the preferential orientation of the chains. During the conference, detailed results shall be presented for the various simulated materials, and the relation between the deformation mechanisms taking place and the material structure will be made clear. The use of global indicators to determine the occurrence of particular phenomena during deformation shall also be presented.

Although the present work focused on the effect of orientation, other factors play similarly important roles and will have to be thoroughly studied, as all of them jointly determine the response of real materials. Eventually, the combination of experiments and computer simulations will allow governing structure-properties relationships to be determined, enabling the creation of knowledge-based polymeric materials with improved properties.

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