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Understanding the micromechanics of deformation of amorphous polymers through molecular dynamics simulations

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Abstract

Amorphous polymers comprise a large group of materials that range from brittle polymers such as polystyrene (PS) and polymethylmethacrylate (PMMA) to ductile ones like polyvinyl chloride (PVC) and polycarbonate (PC). The intrinsic stress-strain response of a glassy amorphous polymer is characterised by an initial elastic regime, a pre-peak non-linear regime, a peak stress, followed by strain softening and strain hardening at large strains. Various constitutive models for glassy amorphous polymers are available, which faithfully model different aspects of the deformation behaviour of these materials. However, most of these models --- in spite of the fact that many of them are micro-mechanically motivated --- contain a large number of parameters that are difficult to determine and whose values evade easy physical justification. Molecular dynamics simulations with a chosen force field allow us to delve deep into the micromechanics of deformation and identify the sequence of events that leave their signatures on the stress-strain response. We show that this information can be used to enrich the existing constitutive models. In particular, we investigate the roles of the evolution of free volume and the entanglement network formed by the macromolecules. We show that the small-strain response is largely governed by how free volume evolves in the material. At larger strains, entanglement slip and disentanglement events govern the extent of plastic strain accumulation and the reversibility of the material upon unloading. The cohesive strength of non-bonded interactions between monomers and the energy barriers associated with torsional flips are the key force-field features governing both the evolution of free volume and the behaviour of the entanglement network. By changing these parameters, we can control the extent of strain softening, hardening, accumulation of plastic strains and reversibility on unloading. The force-field parameters, which are dictated by the macromolecular architecture, can be used to effectively "sculpt" a targeted stress-strain response. We also compare the MD simulations with micromechanically motivated constitutive models to show that many of the parameters inherent in them can be physically motivated and are indeed functions of the underlying atomistic force field parameters.

Keywords:

Glassy amorphous polymers Constitutive modelling Molecular dynamics Free volume Entanglements