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Investigations into the origins of plastic flow and strain hardening in amorphous glassy polymers



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ABSTRACT

In this work, through well designed molecular dynamics (MD) simulations on carefully equilibrated macromolecular ensembles of a generic model of an amorphous glassy polymer, we attempt to understand the origins of plasticity in these materials. In particular, we are interested in the phenomena of post yield strain softening and strain hardening that are typical of these materials. The intrinsic uniaxial stress–strain behaviour is characterized by an elastic part, yield followed by strain-softening and hardening at large strains. Existing constitutive theories of glassy polymers rely on the so called rubber elastic analogy where strain hardening is assumed to be the result of the affine orientation and subsequent stretching of an underlying entanglement network. Using MD simulations and a continuum thermo-mechanical framework, we isolate the plastic free energy associated with the energetic back-stress that governs hardening. We show that the hardening owes its origin to the non-bonded part of the forcefield and is related to the increase in the number of close binary contacts between parts of macromolecular chains that are pushed into close proximity due to compressive deformation. The strain softening is a result of a burst of free volume evolution that accompanies a sudden unstable volume expansion occurring right after yield as the polymer undergoes a deformation induced disordering. This is accompanied by a sharp increase in the room available for changes in dihedral conformations. These conformational changes are mainly responsible for accommodating the plastic deformation as many of them are unable to flip back to their original conformations even after unloading. Finally, by fitting the uniaxial responses obtained from the MD simulations with a standard constitutive model, we show that the barriers between the torsional states govern the small strain behaviour while the strength of the non-bonded interactions govern hardening.

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1. Introduction

With increasing strain, the constant strain rate uniaxial compressive (or intrinsic) stress strain response of most amorphous glassy polymers (e.g., Hasan and Boyce, 1993 for polystyrene, PS; G'Sell et al., 1992 for polycarbonate, PC; Tordjeman et al., 1997 for polymethyl methacrylate, PMMA) exhibits a linear elastic region, prominent strain softening after yield, almost perfect plasticity and finally steep hardening. The extent of softening (also called the 'yield drop') at small strains as well as the hardening at large strains depend on the macromolecular architecture. The extent of the yield drop as well as the hardening is technologically important as the former leads to localisation of strains into thin bands while the latter stabilises them (Lai and Van der Giessen, 1997). For instance, intrinsic response of PC shows a small yield drop followed by a steep hardening while PS shows a sharper yield drop followed by a milder hardening (van Melick et al., 2003) leading to

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significantly different deformation and fracture behaviour in these two materials. Moreover, yield drop and hardening also depend on the applied strain rate, hydrostatic stress and test temperature. The rate, temperature and pressure induced subtleties in the yield drop and hardening responses have been well characterized for almost all important polymers. However, the mechanistic origins of plasticity in these materials in general and the reasons for the yield drop and hardening in particular, are not yet clear. We start by discussing the major points of view that presently exist.

Attempts at providing mechanistic explanations for the elasto-plastic behaviour of these materials date back to [Ree and Eyring \(1955\)](#) and [Robertson \(1966\)](#). The former, based on the idea that yielding is achieved by surmounting the activation energy barrier for the sliding of a segment of a macromolecular chain over others, is able to describe the variation of the yield stress with temperature for a number of polymers ([Bauwens-Crowet et al., 1969](#)). The [Robertson \(1966\)](#) model, on the other hand, connects yielding to activation of conformational jumps on the main chain in parts of the macromolecules. In-situ Fourier transform infrared experiments on thin films of PS have shown that ([Theodorou and Suter, 1985](#); [Xu et al., 1989](#)) there indeed is a sharp increase in the number fraction of certain conformers around the yield point. More recent investigations have pointed out that yielding in a range of amorphous polymers seem to be related to the secondary β relaxations. In fact, many of the molecular motions that are responsible for the β relaxations in commercial polymers have been identified ([Rana et al., 2005](#)). It has been postulated ([van Breemen et al., 2012](#)) that the yield drop results from an interplay between molecular motions related to both the α and β transitions and correspondingly involves two different activation energies.

Alternate to the Eyring approach, another class of models seek to explain yield and strain softening behaviour of polymers. Interestingly, the yield drop in amorphous polymers is a feature of the stress strain response that is also seen in a metallic glasses ([Argon, 1979](#)). In metallic glasses, the carriers of plasticity are believed to be the so-called 'shear transformation zones' (STZ) which are clusters of atoms that undergo intense rearrangement under the application of stress. These regions have atomic environments with liquid-like character ([Cohen and Grest \(1981\)](#)) and in case of most metallic glasses, are about 30 nm³ in size ([Argon, 2013](#)). The idea has been extended by Argon and co-workers to the small strain response of amorphous polymers where, the volume of the shear transformation zone is significantly larger. Using the idea that plasticity in polymers proceeds by the proliferation of liquid like STZs, [Argon \(2013\)](#) was able to model the yield and the yield drop for annealed and quenched PS. The underlying parameters in the model for the compressive stress variation with plastic strain involves a measure of the STZ size which is about 4 orders of magnitude larger than in case of metallic glasses ([Argon and Bessonov, 1997](#)). Also, the liquid like zones make up around 50 % of the volume of the polymer when it reaches the perfectly plastic state. Monte Carlo simulations by [Mott et al. \(1993\)](#) and [Hutnik et al. \(1993\)](#) lend credence to this idea. They have shown that deformation of small macromolecular ensembles proceeds through sudden bursts of large shear activity involving a small number of segments in a chain. Experimental studies of small strain deformation of a number of linear polymers by [Shenogin et al. \(2004\)](#) provide evidence of the nucleation, growth and coalescence of STZs around the yield point. The proliferation of STZs is related to the increase in free volume that provides room for the drastic transformations to take place. The size and distribution of free volume within a glassy polymer sample has been determined through positron annihilation lifetime spectroscopy ([Kobayashi et al., 1994](#); [Cangialosi et al., 2005](#)). A model for rate dependent yield and strain softening can also be formulated from the knowledge of the distribution of free volume within the polymer coupled with the assumption that it is distributed in the same manner as the local strain ([Spathis, 2008](#)).

A number of mechanistic explanations for the hardening of glassy polymers at large strains have also been proposed. Many of these theories are based on the fact that polymer chains are held together by unbreakable topological constraints called entanglements which are 'frozen in' when the polymer is cooled from the melt state. The hardening is believed to be a result of the segments between entanglements being pulled taut by the imposed stretch, which results in the increase in free energy due to reduction in configurational entropy. Since the idea is similar to that employed in rubber elasticity where the cross-links play the role of the unbreakable entanglements, we will henceforth refer to this as the 'rubber elastic analogy' to hardening. The rubber elastic analogy (e.g. [Haward and Thackray, 1968](#), [Boyce et al., 1988](#), [Wu and Van der Giessen, 1993](#), [Ames et al., 2009](#)) derives rigorously from the fact that the segments sample the Langevin or Gaussian distribution of end-to-end distances as they deform and has been successful in fitting the hardening part of the uniaxial response. However, completely phenomenological descriptions of hardening (e.g. [Gent, 1996](#)) are also known to provide equally good fits. Such phenomenological models for strain hardening (as opposed to models that are based on the rubber elastic analogy) have been successfully used in recent constitutive frameworks ([Anand et al., 2009](#) and [Ames et al., 2009](#)). Also, [Li and Buckley, 2010](#) have suggested that hardening in polymers can be modelled through stretch induced anisotropic viscoplasticity in small flow units dispersed within the polymer volume.

A number of issues have been pointed out in connection with the rubber elastic analogy. Two important parameters that enter the model for hardening are N and C_R which are the average number of 'links' making up a segment between two adjacent entanglements and the hardening modulus. The latter is given as $C_R = nk_B T$, where n is the volume density of links, k_B the Boltzmann constant and T the temperature. Recent MD simulations on macromolecular systems with various degrees of atomistic detail ([Hoy and Robbins, 2007](#); [Hoy and Robbins, 2008](#); [Mahajan and Basu, 2010](#)) have pointed out that, if a link is identified with a monomer, N (which now becomes the 'entanglement length' or the number of monomeric units between adjacent entanglements) turns out to be lower than that obtained from measurements of plateau modulus of the corresponding melt. In other words, the number of links between entanglements N is not the same as the entanglement length N_e measured for the corresponding melt. The hardening modulus required to obtain a good fit is also much lower than what is obtained from realistic entanglement densities. Moreover, the modulus C_R is proportional to temperature whereas experiments (e.g. [van Melick et al., 2003](#)) show that they decrease with temperature. Recent simulations and experiments

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