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Molecular Mobility in Deforming Polymer Glasses

Theories and Applications

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To David M. Parks on his recent 70th birthday.

Preface

Plastic deformation in glassy polymers and chain mobility in polymer melts are usually studied under two fields of specialization: continuum plasticity and polymer physics. However, the molecular motion associated with plastic deformation in polymer glasses is a key ingredient to gain a fundamental understanding of the mechanical behavior of polymers at macroscopic and microscopic levels. This monograph attempts to bridge the gap between these two scales by undertaking a unified outlook at an introductory level, provides the necessary background in polymer physics and polymer mechanics, and discusses the topics of molecular mobility accompanying macroscopic inelastic deformation in glassy polymers.

Care is taken so that the content caters to an audience with diverse backgrounds. This monograph focuses primarily on the class of glassy polymeric materials; however, references to other materials are provided only if relevant or necessary. Despite some qualitative similarities with glassy polymers with regard to local microscopic structural rearrangements of atomic clusters during inelastic relaxation, I do not pursue the discussions on metallic glasses because they generally exhibit much less ductility. The topics of material mechanics and enhanced polymer mobility in case of semi-crystalline polymers are also not taken up primarily because there are no "smoking gun" direct applications of deformation-induced mobility in this class of materials. In the solid state, the plastic deformation in semi-crystalline polymers requires activation of slip systems within crystalline domains, or even twinning or martensitic transformations in the presence of surrounding amorphous interphases, which makes the issue of deformation-induced mobility more intricate. At high degrees of crystallinity, semi-crystalline polymers are brittle. Therefore, without pronounced ductility, the deformation-induced mobility will be severely restricted. Moreover, blending of crystalline polymers with additives to enhance deformation-induced mobility for bonding or other applications (as discussed in this monograph) will likely disrupt the internal crystalline structure and render a behavior similar to that of amorphous materials. Notwithstanding the current state of affairs, deformation-induced mobility and its applications in semi-crystalline polymers remain to be investigated.

This monograph is expected to facilitate an introduction to academic coursework and research on the physics, mechanics, and plasticity in the context of glassy polymers. It is also well-suited as supplementary reading in a graduate-level course on the mechanical behavior of polymers. Although the treatment is kept quite brief, I have provided several elementary concepts that unify different fields so that readers from different disciplines can understand this topic, and researchers, students, and practitioners can apply the concepts of the mechanics, plasticity, and diffusion of polymers to various engineering applications. I foresee the central topic of this monograph, deformation-induced bonding, as an upcoming and independent field, with promising areas of research and applications in modeling and simulations at the molecular and continuum levels, and advanced analytical characterization. Open questions in this field of research are discussed and emphasized throughout the text.

Due to the complexity of the molecular-level processes associated with the continuum-scale plastic deformation in polymers, much to my disappointment, at this stage there are no exact, deterministic, and provably correct experimental means or molecular-level theories that precisely reveal all molecular-level events and quantitative characteristics of motions that occur during large strain plasticity in polymers. Nuclear magnetic resonance (NMR) has emerged as a powerful tool in revealing certain dynamical relaxation characteristics in polymers. Other techniques, such as small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), Raman spectroscopy, and transmission electron microscopy (TEM), have been used judiciously to study the microstructure (in situ or post-deformation) for inferring structural changes. However, complete molecular-level understanding of deformation processes is far from complete. With advances in high-performance computing, atomistic and molecular simulations have started having a crucial role in providing plausible molecular descriptions associated with the observed macroscopic behavior. Limitations on accessible timescales and length scales made feasible through simulations (even with the most powerful computing platforms), and the unavailability of exact and direct experimental means for exhaustively monitoring molecular-level activity for each polymer molecule with complete precision in an arbitrary solid-state glassy deformation, are major challenges. We caution that, in general, mechanistic inferences drawn from molecular-scale simulations or experiments of glassy polymers should be considered as suggestive, and care should be taken before drawing exacting conclusions for various reasons.

The underlying challenge in any molecular modeling associated with the plasticity of glassy polymers stems from the fact that a polymer glass is in a non-equilibrium state. Even prior to deformation, the state of the polymer molecules is not certain (i.e., it is dependent on the processing history, and the subsequent deformation states themselves are not in a thermodynamic equilibrium). This characteristic of polymer glasses is in contrast to polymer melts or polymer solutions, whereby modeling of molecular motion in a thermodynamic equilibrium (with appropriate assumptions and approximations) has been tractable and shown some remarkable successes (e.g., for predicting scaling laws for dependence of viscosity or diffusion coefficients on the molecular weight). Unless direct and definitive means of probing molecular-level activities are established and fully

verified, deciphering precise molecular information during plastic deformation will remain unsolved. In spite of this predicament, molecular models, theories, experimental techniques, and simulations that can explain observable findings are useful from a conceptual perspective.

With this background, I have found no single monograph that focuses on deformation-induced molecular mobility in polymer glasses in a detailed and consistent manner while covering and linking the relevant, elementary, and interdisciplinary ideas. There are articles and book chapters available on this topic, but they are not self-contained or tutorial in nature. Most of the excellent textbooks on the mechanical behavior of polymers do not focus on the significance and mechanisms underlying deformation-induced mobility. What is also missing is a holistic viewpoint that connects critical concepts in polymer physics, polymer mechanics, continuum plasticity, and molecular mobility in a simplified (yet complete) manner. It is with this goal in mind that this short project was undertaken. However, due to the limited scope of this monograph, references and discussions on several important works in the physics, mechanics, and material modeling of polymers have been undesirably omitted. Similarly, detailed modeling of the mechanical behavior of polymers, continuum mechanical frameworks for large-strain plasticity, numerical algorithms, and extensively available test data have not been discussed. It is expected that, after reading this monograph, readers will be able to study related topics in detail by following pointers to external references.

This monograph is based on the research work that started at the Massachusetts Institute of Technology (MIT, Cambridge, MA, USA). Its success was truly a result of superb technical guidance provided by Professor David M. Parks. David deserves the credit for identifying and defining the phenomenon of sub-glass transition temperature (T_g), solid-state, plasticity-induced bonding based on the experimental results submitted by me as part of a term-project report in a graduate class at MIT. David is acknowledged for educating me on the plasticity and mechanics of polymers, for which (and many other things) I am truly grateful! David's authority, combined with simplicity, elegance, and clarity, has been a continual source of inspiration for this and related work(s). His unassuming, kind, and warm persona can only be overshadowed by unfathomable depths of his true knowledge and unmatched natural brilliance. This monograph has been assembled in the spirits to celebrate David's recent 70th birthday. It is a tiny tribute by a former student to his teacher. It is expected that the insights offered through this monograph will aid wide applications involving polymer adhesion (explicitly or implicitly). I credit that success to David, with whom an interesting and enlightening discourse has continued on these (and related) matters.

Contributions by the late Professor Ali S. Argon and colleagues at MIT on the mechanics and continuum plasticity of polymers (which essentially laid the foundation for the modern continuum computational plasticity of polymers), and in part for this work, are acknowledged. Professor Lallit Anand's coursework and study material on continuum plasticity at MIT is acknowledged: it provided a formal exposition of this field to me in my formative years. Beginning recently, discussions with Professor Gregory C. Rutledge from the Chemical Engineering

Department at MIT on molecular simulations are appreciated. Some of those discussions and exchanges made their way into this monograph and shaped it, and are acknowledged.

Nikhil Padhye

Contents

Chapter 1
Polymer Physics and Dynamics of Polymer Melts

Abstract The random motion of a flexible molecular chain floating in a solvent or a melt can itself be quite complex. The discussion in this chapter starts with some basic concepts of an ideal polymer chain. It is then followed by classical models describing the dynamics and diffusion of polymer chains applicable to polymer melts. This chapter's main objective is to contrast the differences between the mobility of polymer chains in melts (or solvents) and the kinetically trapped glassy state.

1.1 Introduction

Polymers are commonly referred to as macromolecules because they are large molecules comprising smaller repeating units (monomers) which are bonded covalently. Depending on the arrangement of monomers, the polymers can be categorized as linear, branched, or crosslinked. In linear polymers, the monomer units are repeated along the backbone of a polymer chain. Branched polymers have branches of molecules that are covalently bonded to the main chain. In crosslinked polymers, the molecular entities of one polymer chain are covalently bonded to that of another polymer chain, thereby giving it a network structure. Elastomers contain loosely crosslinked networks, whereas thermosets have a high degree of crosslinked networks. Thermosets degrade upon heating, whereas thermoplastics (which do not contain crosslinks) melt upon application of heat. For other types of classifications in polymers see [29]. The molecular architecture of a polymer directly controls its physical and mechanical properties, so special attention must be given to it for describing polymer properties. The topics discussed in this monograph are focused primarily on linear polymers.

The molecular-level activity of polymer chains is dependent (among other things) upon the physical state of the polymer (i.e., whether the polymer is in the solid state or in a melt or solution). The concepts of solid-state glasses are discussed in greater details in the next chapters. However, let us start with discussion of the

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