Synopsis of the thesis on

Out of equilibrium dynamics in polymers near glass transition

Submitted to

The Maharaja Sayajirao University of Baroda

For the degree of

Doctor of Philosophy in Physics

By

Shipra Bhatt

Under the guidance of

Dr. Debjani Bagchi

ASSISTANT PROFESSOR
DEPARTMENT OF PHYSICS

Introduction

Glasses and the glass transition

Glasses are materials with mechanical rigidity similar to crystalline solids but they lack long-range periodic order. The glass transition in general, is the change from equilibrium fluid state to non-equilibrium disordered solid state[1,2]. When a material is cooled below its freezing point, the molecular motion slows down but if the material is cooled sufficiently fast, crystallization can be avoided and the material becomes glassy[3]. The glassy state is a dynamically arrested state where the material does not relax in experimental timescales, the material's structure appears to be frozen. The system is said to have fallen out of equilibrium and it slowly evolves towards an equilibrium state[1,2,4]. In such far from equilibrium states, the physical properties are found to evolve with time and this phenomenon is known as ageing[5]. The glass transition phenomenon leads to a drastic increase of characteristic molecular relaxation times, and orders of magnitude increase in viscosity[2,3,5–7]. Therefore, at the glass transition temperature, the material becomes too viscous to flow on experimentally realizable timescales.

Dynamic slowdown

Since the viscosity is extraordinarily sensitive to temperature, the viscosity dependence on temperature is well understood by the Arrhenius relation given by $\eta = A\, exp\left({-E_a}/{k_B T}\right)$, where E_a is the activation energy and k_B is Boltzmann constant. Some liquids show a more pronounced viscous slowdown leading to deviations from the Arrhenius behavior which is well described by Vogel Fulcher Tamman relation, $\eta = A\, exp\left({DT_0}/{(T - T_0)}\right)$, where A and D are temperature independent and T_0 is the fictive temperature[2]. Depending upon the viscosity and relaxation time behavior, Angell has proposed a useful classification of glassy materials as strong and fragile where the viscosity and relaxation times of the former follow Arrhenius fashion and the fragile liquids show deviations from the Arrhenius behavior and in many cases follow the Vogel Fulcher Tamman relation[2,5,8]. The categorization of glasses as strong and fragile is not just related to the mechanical properties of the glass but it is also based on a short ranged structural order which has been responsible for the origin of dynamic slowdown[9]. Various model systems have also observed medium ranged structural order associated with the glassy dynamics[8,10,11]. Experimental and computational evidence shows that the dynamic slowdown has a molecular origin and it is associated with structural ordering at the molecular level[11–16].

Dynamic heterogeneities

When supercooled liquids are allowed to relax, they possess regions of fast and slow relaxations which represent heterogeneous ordering at the molecular level[17]. Molecular dynamics simulations on glass formers have observed that particle displacements in a time scale corresponding to structural relaxation is highly heterogeneous and the particles with similar mobility cluster together forming separate regions of high mobility and low mobility such that there is a correlation between the region of high/low mobility which is usually used in determining the dynamic correlation lengths[7,18,19]. Several theories have been proposed to develop a framework for this dynamical behavior like, the presence of cooperatively rearranging regions (CRRs), growth of a region with solid molecular interaction, hierarchical interactions of mobility excitations[20–22]. Molecular dynamics simulations have also shown that the dynamic heterogeneity is associated with a short ranged and medium ranged structural order which is highly system dependent[13]. There are evidences which show that the dynamic heterogeneity is associated with a structural component underlying the dynamic susceptibility,[23], but the possible link between the local structure and the dynamic heterogeneity and detailed experimental studies on systems showing dynamic heterogeneities is still lacking.

Effect of glassy state on macroscopic properties

The fundamental processes occurring at the microscopic level in the glassy materials has a prominent effect on the macroscopic properties of the material. The connection of relaxation times and molecular pair interaction parameters to macroscopic properties has been extensively pursued and shown that yield behaviour of miscible blends can be predicted from knowledge of the compositional dependent relaxation time and strength of volume interactions[24–26]. The macroscopic properties of the polymer glass are affected by the molecular orientation in the glassy state which causes macroscopic anisotropy evidenced in thermal conductivity, thermal expansion, elastic modulus, refractive index, etc [15,27]. Because residual stress as well as flow-induced molecular orientation affects macroscopic properties, prediction of residual molecular orientation in glassy polymers is important. The relaxation behaviour of glasses can also be affected by the presence of confined geometry. It has been observed that the conformational changes affect the packing density and chain dynamics (mobility) in the confined interfaces/ surface as compared to the bulk glass[28–31]. Therefore, in order to design materials with better mechanical properties it is important to understand the microscopic / molecular origin of the anomalous behaviour observed.

Applications of glassy polymers

Polymers have wide-ranging applications, ranging from gas separation to corrosion resistant coatings to drug delivery systems. With the development of technology, glassy state of polymers is an important concern to develop devices with improved performance because studies have shown that properties like the non-periodic order of glassy system helps in increasing the overall conductance and transport characteristics[32,33]. The glassy and rubbery state of polymers has also been beneficial in the development of biosensors, neutron detectors and membranes for gas separation[34]. Dynamical slowing down of relaxation dynamics affects not only the mechanical properties but also other macroscopic properties like dielectric response, crucial for device performance especially in charge storage applications. Moreover, the widespread use of non-biodegradable polymers like polyethylene which is an environmental hazard, it has become important to look for alternatives which can be environment friendly.

Rationale

Unveiling the behavior of disordered systems has been an important concern since decades because the anomalous dynamics like structural relaxation and cooperatively rearranging regions at the microscopic scale has been found to control the macroscopic properties like dielectric and mechanical response of the system. Heterogeneous plastic deformation, as well as physical aging has a microscopic origin. Simulations have shown that the glassy dynamics is governed by molecular scale mobilities which can affect mechanical response of the material[35–37] . Despite years of research to understand the origin of the glassy dynamics in disordered system, there has been a limited amount of experimental work to support the theoretical predictions. This study aims to experimentally understand the dynamics in disordered system, i.e., polymers near their glass transition temperature. The intriguing applications of glassy polymers ranging from gas separation to corrosion resistant coatings to drug delivery systems is due to its disordered nature which leads to increased conductivity, permeability and mechanical resistance. Most applications use non-biodegradable polymers which are major source of environmental pollution. The need of the hour is to develop methods to replace more environment friendly biodegradable polymers in place of non-biodegradable polymers. This necessitates a comparative structure-property analysis of biodegradable polymers with respect to and polyethylene. The work presented in this thesis addresses these issues by experimental studies on biodegradable as well as nonbiodegradable polymers at the molecular scale, micro-scale, and macroscopic scale with the objectives presented in the following section. The chapters in the thesis addresses these objectives, and the results obtained are summarized in the following sections.

Objectives

1. Comparison of thermal and mechanical response of biodegradable polymer with polyethylene.
2. Study of relaxation dynamics of a glassy polymer near the glass transition temperature.
3. Measurement of dynamic heterogeneities in the glassy state of a polymer.
4. Methodology development to study micro-scale diffusion dynamics of polymers.

Results

Chapter 1 Comparison of biodegradable polymers with polyethylene at the macroscopic and molecular scale in response to mechanical and thermal perturbations.

With the growing plastic pollution in the environment which is mainly caused due to polyethylene-based products, it has become important to look for alternatives which can replace the traditional non-biodegradable polyethylene with a more environmentally friendly polymer. in order to look for an alternative to polyethylene a very important factor which cannot be ignored is the mechanical compatibility. In this chapter we suggest a biodegradable polymer polypropylene carbonate which possesses mechanical features comparable to the rigid high-density polyethylene as well as elasticity and extensibility comparable to highly plastic linear low-density polyethylene, as revealed from tensile testing experiments. The response to tensile stress of the polymer films reveals that the macroscopic mechanical properties of drop casted polypropylene carbonate films match the industry processed polyethylene films.

Along with the response to mechanical perturbations, a response to thermal perturbations for the polymer films was studied using Raman scattering because Raman scattering is a technique which gives information about all the molecular modes present within the polymer. the response to thermal perturbation using Raman scattering revealed the presence of molecular mobility in the polymer films on being exposed to the thermal cycle. The decrease in the crystalline character of polyethylene films after thermal cycling also supported the presence of molecular mobility. The variation in the Raman peak parameters which indicates the presence of molecular mobility was found to have a strong correlation with the tensile properties which suggests that there is interrelation between the molecular scale variations which can affect the macroscopic mechanical properties of the polymer films. Therefore, the molecular scale mobility induced can thus become an important factor in determination of the macroscopic properties which needs to be understood further for the glassy state of the polymers.

Chapter 2 Thermal relaxation of polyvinyl acetate near the glass transition temperature – a micro-Raman study.

This chapter attempts to decipher the nature of glass transition in a polymer film through a novel approach of looking at the molecular scale relaxations after two different (slow and fast) thermal perturbations using Raman Scattering experiments. Raman scattering is a vibrational technique which decouples the molecular modes of the polymer as a result of which the vibrations of individual molecular modes present in the main chain as well as the side branch of the polymer can be analyzed separately and their relaxation mechanism can be traced. The Raman modes are spectrally separated for main chain and side chain of the polymer but the response to thermal cycle reveals a string inter-mode correlation between different modes irrespective of their presence in main chain and side branch of the polymer implying the cooperative behavior of the molecular motion in the main and side branch of the polymer. The presence of hysteretic behavior in Raman peak parameters during thermal cycling reveals a mosaic of cooperative regions with different molecular conformational domains. Our experimental observations also provide evidence to the presence of cooperatively rearranging heterogeneous domain which supports the Random First order theory (RFOT) in a polymer glass.

Another important observation of the present study is a clear distinction between the relaxations of polymer film and unprocessed state of the polymer. Although the film is drop casted from polymer solution and is reasonably thick enough to minimize the confinement effects, the molecular relaxations show deviation in the relaxation behavior from VFT in unprocessed polymer to Arrhenius in polymer film. There is also a deviation from the caging relaxation to the long segmental relaxation in polymer film on crossing the glass transition temperature during thermal cycling. Overall, this chapter lays importance of studying the response to thermal perturbations which can be an important factor during applications like polymer coatings which endure thermal variations in addition to the presence of glassy state which can change the friction, adhesive properties or tribology of the film which is an important consideration in advanced polymer-based lithography.

Chapter 3 Experimental measure of dynamic heterogeneities and correlations near the glass transition temperature

The presence of cooperatively rearranging regions with heterogeneous character is evident from the previous chapter. This lays the ground for the presence of dynamic heterogeneities in the glassy state of polymer. To study and experimentally observe the presence of dynamic heterogeneities, polymer film was exposed to thermal quench passing through the glass transition temperature in order to drive the system in its glassy state. A 2-D map of the polymer film using Raman scattering revealed the presence of heterogeneous domain with variable intensity signifying the presence of domains with less and high contribution from the respective molecular modes. These heterogeneous domains evolved after quenching through the glass transition temperature which was evident from the 2-D contour map of the polymer film. The growth of the heterogeneous domains after thermal quench is evidence of the presence of dynamic heterogeneities in the glassy state of a polymer film. This type of heterogeneous behavior has been previously observed in the mean square displacement of glass formers via molecular dynamics simulations where heterogeneous domains of variable mobility are observed in the glassy state[2] .

The dynamic heterogeneities in the polymer film after thermal cycling show cooperativity between the dynamically relaxing domains. The molecular modes present in the Raman spectrum of polymer film as well as in the unprocessed state showed weak to strong correlations as a function of the thermal cycles exposed. The presence of correlations is a signature of the cooperative behavior of the relaxing heterogeneous domains. We have attempted to obtain a length scale of these correlating domains by defining a susceptibility, calculated from Raman mode intensities.

Chapter 4 Fluorescence recovery after photobleaching experiments to study micro-scale polymer dynamics.

The development of application-specific polymer films require study of micro-scale mechanical response in addition to macroscopic mechanical response. In order to achieve products with tunable mechanical properties, polymers have been reinforced with several nanoparticles like silver, gold, silica, cellulose, clay, carbon nanotubes etc. But the presence of these filler not only affects their macroscopic mechanical properties but it also affects the micro-scale mechanical response. In order to have a desired and compatible product with any polymer it is therefore important to look at the micro-scale mechanical response. In this chapter we propose a methodology to study the micro-scale mechanical response of the filler reinforced polymer matric using a microscopic technique known as Fluorescence Recovery after photobleaching (FRAP). Using this technique, the micro-scale mechanical response is studied by measuring the diffusion time of the fluorescent probes in the polymer matrix. The increase in concentration of the polymer increases the diffusion time of the fluorescent probes and the micro-scale diffusion coefficient follows a rouse scaling. The addition of nanofillers like cellulose and bentonite leads to inhomogeneities and aggregation of the filler particles leading a slower and more heterogeneous diffusion of fluorescent probes with bentonite nanoparticles when compared to cellulose nanofibers.

A simultaneous structural analysis technique is developed from prebleached FRAP images, and compared to structural analysis with small angle X ray scattering (SAXS) experiments. The static microstructure studies reveal the presence of depletion interaction induced structuring in the polymer matric on addition of bentonite nanofillers with an increase in the size of aggregates on increasing the concentration of polymer or bentonite nanoparticles. This chapter demonstrates that FRAP is an efficient technique to study the micro-scale transport properties in polymer matrix as well as analyze the effect of addition of nanofillers in polymer matrix. It can also detect microstructural heterogeneities in the polymer matrix along which can potentially influence the macroscopic mechanical properties of the polymer.

Conclusions and future perspectives

A fundamental question in glassy physics is the relationship between the structure and properties of glassy systems. The study of glass transition phenomenon using Raman spectroscopy provides evidence to the molecular origin of the glass transition phenomenon. The tracking of configurational changes and molecular mobility during the thermal cycling of a polymer films establishes a connection between the glassy dynamics and the molecular motions in the polymer. The study of response to thermal perturbation in glassy polymer shows that the relaxation behavior of a polymer films shows a transition from the caging dynamics to cooperative segmental dynamics on crossing the glass transition temperature which is an important outcome for glassy physics. The cooperativity in the glassy state of polymers also provides evidence to the presence of cooperatively rearranging regions which satisfies with the Random First order theory. The presence of dynamic heterogeneities in a 2-dimensional mapping of polymer films in glassy state establishes an important conclusion that the glass transition phenomenon is accompanied with the dynamic heterogeneities not only at the microscopic level but also at the molecular level.

Another important outcome of the present study is the study of microscopic mechanical properties which emphasizes the importance of molecular interactions which has an impact on the structure of the polymer matrix, and micro-scale diffusion dynamics. The study also provides a methodology to use the FRAP technique to study the micro-mechanical properties and a simultaneous structural analysis on addition of filler particles in the polymer matrix. The current work has studied the effect of micro structuring like aggregation due to the presence of interactions within the polymer matrix on the macroscopic mechanical properties.

Thus, for better applicability of any polymer and for the development of new polymer-based products it is important to look at the molecular as well as microscopic properties in order to achieve desirable macroscopic properties. Overall, this study lays out the importance of looking at different length scales to get an in depth understanding of glassy dynamics.

References

(1) Debenedetti, P. G.; Stillinger, F. H. Supercooled Liquids and the Glass Transition. *Nature* **2001**, *410* (March), 259–267.

(2) Berthier, L.; Biroli, G. Theoretical Perspective on the Glass Transition and Amorphous

Materials. *Rev. Mod. Phys.* **2011**, *83* (2), 587–645.

(3) Ediger, M. D.; Angell, C. A.; Nagel, S. R. Supercooled Liquids and Glasses. *J. Phys. Chem.* **1996**, *100* (31), 13200–13212.

(4) Fukao, K.; Miyamoto, Y. Slow Dynamics near Glass Transitions in Thin Polymer Films. *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.* **2001**, *64* (1), 9.

(5) Angell, C. A. Formation of Glasses from Liquids and Biopolymers. *Science (80-.).* **1995**, *267* (5206), 1924–1935.

(6) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in Glassforming Liquids and Amorphous Solids. *J. Appl. Phys.* **2000**, *88* (6), 3113–3157.

(7) Ediger, M. D. Spatially Heterogeneous Dynamics in Supercooled Liquids. *Annu. Rev. Phys. Chem.* **2000**, *51*, 99–128.

(8) Metatla, N.; Soldera, A. The Vogel - Fulcher - Tamman Equation Investigated by Atomistic Simulation with Regard to the Adam - Gibbs Model. *Macromolecules* **2007**, *40*, 9680–9685.

(9) Merrick, M. M.; Sujanani, R.; Freeman, B. D. Glassy Polymers: Historical Findings, Membrane Applications, and Unresolved Questions Regarding Physical Aging. *Polymer (Guildf).* **2020**, *211*, 123176.

(10) Phys, J. C.; Scalliet, C.; Ninarello, A.; Scalliet, C.; Ninarello, A. Does the Adam-Gibbs Relation Hold in Simulated Supercooled Liquids ? Does the Adam-Gibbs Relation Hold in Simulated Supercooled Liquids ? **2019**, *084504* (June).

(11) Karmakar, S.; Dasgupta, C.; Sastry, S. Growing Length Scales and Their Relation to Timescales in Glass-Forming Liquids. **2014**.

(12) Karmakar, S.; Dasgupta, C.; Sastry, S. Growing Length and Time Scales in Glass-Forming Liquids. *Proc. Natl. Acad. Sci.* **2009**, *106* (March), 3675–3679.

(13) Tah, I.; Sengupta, S.; Sastry, S.; Dasgupta, C.; Karmakar, S. Glass Transition in Supercooled Liquids with Medium-Range Crystalline Order. *Phys. Rev. Lett.* **2018**, *121* (8), 85703.

(14) Chaudhuri, P.; Sastry, S.; Kob, W. Tracking Heterogeneous Dynamics during the α Relaxation of a Simple Glass Former. *Phys. Rev. Lett.* **2008**, *101* (19), 1–4.

(15) Anstine, D. M.; Strachan, A.; Colina, C. M. Effects of an Atomistic Modeling Approach on Predicted Mechanical Properties of Glassy Polymers via Molecular Dynamics. *Model. Simul. Mater. Sci. Eng.* **2020**, *28* (2).

(16) Barrat, J.; Lyulin, A. Molecular Dynamics Simulations of Glassy Polymers. **2010**.

(17) Biroli, G.; Garrahan, J. P. Perspective: The Glass Transition. *J. Chem. Phys.* **2013**, *138* (12).

(18) Szymoniak, P.; Madkour, S.; Schönhals, A. Molecular Dynamics of the Asymmetric Blend PVME/PS Revisited by Broadband Dielectric and Specific Heat Spectroscopy: Evidence of Multiple Glassy Dynamics. *Macromolecules* **2019**, *52* (4), 1620–1631.

(19) Chaudhuri, P.; Horbach, J. Structural Inhomogeneities in Glasses via Cavitation. *Phys. Rev. B* **2016**, *94* (9), 1–10.

(20) Doi, M.; Edwards, S. The Theory of Polymer Dynamics. ... *University Press*. 1986.

(21) Das, R.; Tah, I.; Karmakar, S. Possible Universal Relation between Short Time β - Relaxation and Long Time α -Relaxation in Glass-Forming Liquids. *J. Chem. Phys.* **2018**, *149* (2).

(22) Calandra, P.; Pieruccini, M.; Sturniolo, S. The Emergence of Cooperative Dynamics in Polymers as an Effect of Conformational Restrictions: The Case of Crystallization and an Example on Heterogeneous Confinement. *Thermochim. Acta* **2011**, *522* (1–2), 135–143.

(23) Balbuena, C.; Mariel Gianetti, M.; Rodolfo Soulé, E. A Structural Study and Its Relation to Dynamic Heterogeneity in a Polymer Glass Former. *Soft Matter* **2021**, *17* (12), 3503–3512.

(24) Hill, A. J.; Tant, M. R. The Structure and Properties of Glassy Polymers: An Overview. *ACS Symp. Ser.* **1998**, *710*, 1–20.

(25) Chow, T. S. Nonlinear Stress-Strain Behavior of Glassy Polymers. *Polym. Eng. Sci.* **1996**, *36* (24), 2939–2944.

(26) Chow, T. S. Glassy State Relaxation and Deformation in Polymers. *Adv. Polym. Sci.*

1992, *103*, 148–190.

(27) Tong, H.; Tanaka, H. Role of Attractive Interactions in Structure Ordering and Dynamics of Glass-Forming Liquids. *Phys. Rev. Lett.* **2020**, *124* (22), 225501.

(28) Monnier, X.; Cangialosi, D. Thermodynamic Ultrastability of a Polymer Glass Confined at the Micrometer Length Scale. *Phys. Rev. Lett.* **2018**, *121* (13), 1–6.

(29) Napolitano, S.; Glynos, E.; Tito, N. B. Glass Transition of Polymers in Bulk , Confined Geometries , and near Interfaces. *Reports Prog. Phys.* **2017**, aa5284.

(30) Adrjanowicz, K.; Winkler, R.; Dzienia, A.; Paluch, M.; Napolitano, S. Connecting 1D and 2D Confined Polymer Dynamics to Its Bulk Behavior via Density Scaling. *ACS Macro Lett.* **2019**, *8*, 304–309.

(31) Cho, S.; Jeong, S.; Kim, J. M.; Baig, C. Molecular Dynamics for Linear Polymer Melts in Bulk and Confined Systems under Shear Flow. *Sci. Rep.* **2017**, No. July, 1–9.

(32) Chatzispyroglou, P.; Keddie, J. L.; Sellin, P. J. Boron-Loaded Polymeric Sensor for the Direct Detection of Thermal Neutrons. *ACS Appl. Mater. Interfaces* **2020**, *12* (29), 33050–33057.

(33) Ghorbani Zamani, F.; Moulahoum, H.; Ak, M.; Odaci Demirkol, D.; Timur, S. Current Trends in the Development of Conducting Polymers-Based Biosensors. *TrAC - Trends Anal. Chem.* **2019**, *118*, 264–276.

(34) Farnam, M.; bin Mukhtar, H.; bin Mohd Shariff, A. A Review on Glassy and Rubbery Polymeric Membranes for Natural Gas Purification. *ChemBioEng Rev.* **2021**, *8* (2), 90–109.

(35) Xu, W. S.; Douglas, J. F.; Xu, X. Molecular Dynamics Study of Glass Formation in Polymer Melts with Varying Chain Stiffness. *Macromolecules* **2020**, *53* (12), 4796–4809.

(36) Alesadi, A.; Xia, W. Understanding the Role of Cohesive Interaction in Mechanical Behavior of a Glassy Polymer. *Macromolecules* **2020**, *53* (7), 2754–2763.

(37) Bulacu, M.; Van Der Giessen, E. Molecular-Dynamics Simulation Study of the Glass Transition in Amorphous Polymers with Controlled Chain Stiffness. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2007**, *76* (1), 1–11.