Chapter 1

Introduction

1.1 Fundamentals of a glass

Glasses represent a unique state of matter which has characteristics similar to solid as well as the liquid state. In general, glasses are materials with mechanical rigidity similar to crystalline solids but they lack long-range periodic order[1, 2]. They are ubiquitous in nature and are widely used in our day-to-day life, yet, the microscopic and molecular origin of the intriguing properties in the glassy state are still uncovered.

The glassy state forms when a material is cooled rapidly below its freezing point from the molten state such that the crystallization of the material is avoided and the material does not achieve the minimum energy, ordered configurational state at an achievable timescale. The system then accesses several local minima on the configurational energy landscape as it evolves towards the crystalline state [1, 2, 3, 4]. The rate of cooling is, therefore, an important parameter during the process of glass formation [3]. The glass transition temperature (T_g) in general is defined the temperature at which the phase changes from equilibrium fluid state to non-equilibrium disordered solid state [5, 6, 7]. Every material has its corresponding T_g below which the material can be found to be in the glassy state. The glass transition phenomenon often carries characteristics similar to the second-order phase transition but there is still a debate on whether it is a kinetic transition or a thermodynamic transition and this is considered to be one of the deepest and unresolved questions of glassy physics [3, 6, 7, 8].

The glassy state is a dynamically arrested state where the material relaxes slowly such that the material's structure appears to be frozen [7]. The system is said to have fallen out of equilibrium and it slowly evolves toward an equilibrium state. The relaxation time of such materials becomes so large that it cannot be measured on an experimental timescale or even that of a numerical simulation [1, 2, 3, 6, 7]. A wide variety of materials ranging from metals to polymers can behave like glass. Semiconductors such as amorphous or nanocrystalline silicon can have glassy states, spin glasses with charge density waves have been discovered [9] and a wide variety of soft matter systems have glassy behavior such as polymer, colloids, gels, emulsions, proteins, etc [10].

So far it has been established that glasses have peculiar properties like the dynamic slowdown of relaxation time, presence of dynamic heterogeneities, etc. which are important to study for the overall understanding of glassy dynamics. But a very important question that follows is whether the dynamical behavior of glasses has any impact on the macroscopic properties of the glass former. The answer to this question is 'yes'. The fundamental processes occurring at the microscopic level in glassy materials have a prominent effect on the macroscopic properties of the material from the mechanical to dielectric and from optical to thermal properties of the material.

1.1.1 Mechanical properties

Determining the mechanical properties like yield, shear, modulus, stiffness, and strength is of utmost importance for the application of any material. When a glassy material undergoes a mechanical perturbation, the microscopic as well as macroscopic properties of the material depart from the ideal behavior and a possible reason for this is the glassy dynamics of the material. The connection of relaxation times and molecular pair interaction parameters to macroscopic properties has been extensively pursued and shown that yield behavior of miscible blends can be predicted from knowledge of the composition-dependent relaxation time and strength of volume interactions [11, 12]. 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 [13]. 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 behavior 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 [14, 15]. Recent studies mainly molecular dynamics simulations have shown that increasing the chain stiffness of an amorphous polymer increases its T_g, also the diffusion coefficient 'D' is dependent on the polymer chain length [15, 16]. A decrease in the relaxation time of polymer glass with chain stiffness has also been reported [17]. Monodisperse and polydisperse colloidal gels have faced the evolution of structural and rheological properties during the sol-gel phase transition [18, 19]. Therefore, to design materials with better mechanical properties it is important to understand the microscopic/molecular origin of the anomalous behavior observed.

1.1.2 Dielectric properties

Polymers with tunable dielectric properties like low dielectric loss, high-temperature tolerance, flexibility, etc. are highly desirable for the advancement of the development of next-generation electronic devices. Recent coarse-grained molecular dynamics simulations and experimental studies have found that low T_g polymers have low dielectric properties and also elucidate the structure-property relationship for ionic conductivity of the polymer [20, 21]. Simulations have also suggested that polymers with T_g below ambient temperature have low ionic conductivity limited by salt solubility and dissociation [20]. The dielectric properties also have a temperature dependence, *e.g.*, for epoxy-boron-nitride composites, the dielectric constant and dielectric loss increase on increasing the temperature of the composite material [22]. Simulations and experiments have been conducted to understand the dielectric relaxation of polymers. The dielectric relaxation of a polycarbonate studied at room temperature under strain has been found to resemble the relaxation of an unstretched polymer near T_g [23]. This suggests that even at room temperature, the polymer can be in its glassy state under mechanical perturbations.

1.1.3 Optical properties

It is important to study the optical properties of polymers because absorption processes for amorphous systems have been observed to be different from their crystalline counterparts. An interesting feature is that the non-linear optical properties of glasses have potential applications in the field of light modulation, optical switches, and optical storage devices, which depend on different properties like birefringence, transparency, refractive index, etc. The T_g values for conjugated polymers are correlated with the sub-bandgap optical absorption in a recent study, suggesting the possible role of the interchain contacts between the amorphous domains of the material [24]. The change in optical properties like refractive index has also been used to track the physical aging of the glassy polymers where pronounced aging was reflected in changing refractive index [25, 26]. The development of polymer nanocomposites for tuning the mechanical and dielectric properties also introduces a substantial change in its optical properties, especially absorption and emission which are beneficial for optical sensor applications [24]. The development of polymer nanocomposites can control the dispersion of luminescent particles into a wide range of polymer matrices which can help in the development of dye-sensitive smart optical devices [27].

As evident from the aforementioned studies, the glassy behavior of materials has a definitive impact on the macroscopic properties of the material whether it is the stiffness or the ionic conductivity, or the optical properties of the material. Therefore, the study of the glass transition phenomenon and overall understanding of the anomalous behavior of materials near T_g becomes more important not only from the fundamental point of view but also for the application of the materials.

1.2 Glass transition and Physical Aging

The most generic and ideal definition of a glass transition is the temperature where the liquid solidifies avoiding the long-ranged crystalline order [2, 4]. This definition comes from the temperature dependence of a liquid's volume or entropy which is shown in Figure 1.1 (a) the highest point of the curve, the material is in its liquid state which is also its equilibrium state at a given volume (V) is constant representing the thermal expansion of the liquid. If the system is cooled slower to crystallize the sample then liquid to solid phase transition occurs at a temperature (T_m, the melting temperature). The T_g is often determined experimentally using Differential Scanning Calorimetry (DSC)

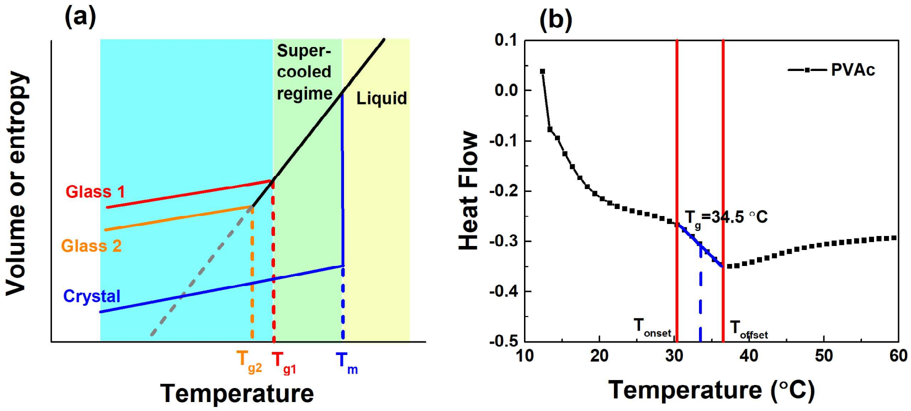

FIGURE 1.1: (a) Schematic representation of the process of glass formation and (b) DSC thermograph of Polyvinyl acetate (PVAc) representing the onset, offset, and transition temperature.

which measures the heat flow during the heating/cooling of the material. The heat flow curve for a polymer, Poly-vinyl Acetate (PVAc) is shown in Figure 1.1 (b) where the onset and offset of the glass transition are shown and the midpoint of these gives the T_g.

When a material is drawn into its glassy state, i.e., below its T_g, the physical properties like volume, enthalpy, modulus, etc. show a behavior different from the equilibrium conditions. This change in the physical properties of glassy material is popularly known as physical aging [28, 29, 30]. In general, physical aging is the evolution of the glassy state as a function of time after quenching (fast cooling). The most common definition of physical aging is the structural evolution of the glassy state. Physical aging is different from chemical aging because physical aging is a reversible process, the material can be brought back into its equilibrium state after slow cooling but during chemical aging, degradation of the material occurs which results in permanent irreversible changes in the material [3, 4].

In a glassy system undergoing physical aging, molecules gradually rearrange themselves to reach a stable thermodynamic equilibrium state, leading to a time-evolution of several properties. The process of physical aging can be observed in the form of a change in the physical properties like specific volume, enthalpy, etc. of the material with time [31]. The relaxation dynamics become slower and slower ith the passage of time during aging [30]. Howevr, there are some recent advancements in the study of physical aging in glassy polymers show that a fast relaxation preceeds the slow relaxing process [32, 33, 34]. Also, the deviation from classical α relaxation is observed when the polymer is taken deeper into the glassy state [35, 36]. Physical aging is always assumed to be at larger time scales and is supposed to be undetectable at a temperature far below the T_g. However, recent studies have detected a short equilibration time at temperatures below T_g [35] which challenges the current understanding of physical aging, thereby making it necessary to study the temperature dependence of physical aging.

1.3 Dynamic Slowdown

The supercooled state Figure 1.1 (a) is a metastable state where the time scale of relaxation (τ_α) increases to many orders of magnitude larger as the T_g is crossed. The increase in τ_α is also accompanied by the increase in viscosity (η) and the relationship between τ_α and η is given by the Maxwell model in which $\eta = G_\infty \tau_\alpha$ where G_∞ is the instantaneous shear modulus which is constant in supercooled regime [3, 6, 7]. Based on the dynamic increase in viscosity, the glass transition can be defined as the temperature at which the liquids are unable to flow and form an amorphous solid called 'glass'.

The supercooled state of liquids has drawn interest for decades not only due to the increase in τ_α but also because of its temperature dependence. Based on the temperature evolution of τ_α, Angell has designed a characteristics plot known as the 'Angell plot' which is used to categorize the glass forming liquids [1]. According to Angell, the temperature dependence of τ_α or η of a strong glass will be driven by activation energy (E_a) and will show an Arrhenius behavior:

$$\tau_\alpha = \tau_0 \exp \frac{E_a}{k_B T} \tag{1.1}$$

In this case, the molecules are required to cross a potential energy barrier for the system to relax. Another category of glasses is fragile glasses, which are exhibited by liquids that have more pronounced viscous slowdown near T_g and they deviate from the Arrhenius behavior. For fragile glass formers, the activation energy increases with a decrease in temperature, and this behavior is known as super Arrhenius behavior [3, 37]. The temperature dependence of τ_α or η of such glass formers is given by Volgel Fulcher Tamman (VFT) relation:

$$\tau_\alpha = \tau_0 \exp \frac{DT_0}{T - T_0} \tag{1.2}$$

The VFT relation suggests that the relaxation time diverges from Arrhenius behavior at a finite temperature T_0 known as fictive temperature which represents the presence of a phase transition and D is the fragility index where smaller D indicates that the glass is more fragile[3, 6]. Recent studies have found that fragility can be correlated with chemical structures in polymers, the studies have shown distinctions in the fragility of the polymer with strong backbones and the ones with bulky side groups [38]. Even during the formation of thin films, the fragility has been found to decrease with increasing confinement ratio for some glass formers [39].

The definition of strong and fragile glass formers is based on the short-range ordering which is present near the T_g [2]. Adam and Gibbs in 1965 designed a model stating that the relaxation time τ_α is controlled by the configurational entropy $S_c(T)$ of the system [40]. When the system is close to T_g, the energy landscape marked with a huge number of energy minima separated by barriers of variable depth which increases on decreasing the temperature. At T_g, the barrier becomes so large that the system remains trapped in one of the minima and the system will evolve following jumps between the minima [41]. According to this interpretation, the entropy of the system can thus be written as $S(T) = S_{vib}(T) + S_c(T)$, and the configurational entropy is dependent on the number of metastable states as $S_c(T) = \log(N_{metastable})$. The Adam Gibbs model, captures the simple idea of entropy dependence of relaxation time given by the following relation [40, 42]:

$$\log(\frac{\tau_\alpha}{\tau_0}) = \frac{1}{TS_c} \tag{1.3}$$

here, τ_0 is the microscopic time scale. The Adam Gibbs theory, therefore, gave the thermodynamic framework to the glass transition phenomenon. The above relation, therefore, justifies that the glass transition phenomenon is a thermally activated transition that involves molecular rearrangement of all molecules in cooperatively rearranging regions (CRRs). The CRRs can thus be defined as a subset of the system which can rearrange into another configuration provided there is a sufficient amount of energy.

The Adam Gibbs model has been successfully tested in various numerical simulations especially performed at a higher temperature for various glass formers [43, 44, 45]. The major drawback with these results is that these simulations have been performed at a temperature range different from the experimentally achievable temperatures. There has also been experimental verification of the Adam Gibbs model for the temperatures close to T_g for a range of materials [46, 47, 48]. Systematic deviations from the Adam-Gibbs relation were also reported for some systems [49, 50] but imprecise entropy measurements or inappropriate time scale determinations have been invoked to rationalize them. Despite various contradictions to the Adam Gibbs model, the entropy dependence of relaxation dynamics and the presence of CRRs in a glass-forming system is undeniable.

1.4 Static and dynamic correlation functions

Another key signature of glass transition is the diverging time scale on approaching T_g which can be seen from the static correlation functions like structure factor S(q) which displays a diverging correlation length related to the emergence of amorphous order given by [2, 3, 7]:

$$S(q) = \left\langle \frac{1}{N}\rho_q \rho_{-q} \right\rangle \tag{1.4}$$

where ρ_q is the Fourier transform component of density given by:

$$\rho_q = \sum_{j=1}^{N} e^{i(q.r_j)} \tag{1.5}$$

with N number of particles in volume V at position r_j of j^{th} particle. The static structure factor, therefore, represents the correlations along the length scales of the particles but it lacks information about the diverging q values. This difficulty vanishes with a dynamic correlation function which is a time-dependent density-density correlation function, also known as scattering function F(q,t) which probes the correlations in density fluctuations of a particle at a wavenumber q over the time t from the following relation:

$$F(q,t) = \left\langle \frac{1}{N} \rho_q(t) \rho_{-q}(0) \right\rangle \tag{1.6}$$

It is an open and debatable question whether the glass-forming material relaxes homogeneously across all regions of the material or whether different regions are relaxing at different time scales. The scattering function F(q,t) measures to what extent the instantaneous configuration will resemble the new configuration at a later time t and the length scale over which the resemblance is measured is given by wavenumber q. The dynamic at the molecular level can be probed by choosing q as the inverse of particle size and the dynamics at the macroscopic level can be probed with q $\rightarrow 0$. Different neutron scattering experiments for supercooled glycerol have revealed that the fast relaxation plateau in F(q,t) is accompanied by another slow relaxation plateau [51]. This is due to the fractional density fluctuations in the frozen intermediate time scales which relax slowly. Such slower relaxations are called α relaxations and they represent the structural relaxation of the glass-forming liquid and the fast relaxations are the β relaxations which are due to the caging of the molecules trapped in the energy minima [7, 52, 53]. As the temperature approaches the T_g, the plateau in F(q,t) will approach towards slower relaxations and increasing time scales which eventually fall out of the experimentally observable time scales. The static and dynamic correlation functions, therefore, provide an idea that the glass transition process undergoes multiple length scales and time scales which grow on approaching T_g.

1.5 Dynamic Heterogeneities

When supercooled liquids are allowed to relax, they possess regions of fast and slow relaxations which represent heterogeneous ordering at the micro and molecular level [53]. 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, characterized by dynamic correlation lengths [54, 55, 56, 57]. Therefore, dynamic heterogeneity can be defined in the form of heterogeneous structural relaxation in clusters of cooperatively rearranging regions (CRRs) on approaching T_g. Such mobile domains are variable in both space and time thus giving rise to non-trivial spatio-temporal fluctuations. These fluctuations have also been analyzed in the form of a quantity called the dynamic susceptibility ($\chi_4(t)$) which quantifies the amplitude of spontaneous fluctuations around the average dynamics [3]. To characterize these fluctuations, it is important to resolve the dynamics in both space and time and quantify deviations from the average behavior. For this, the four-point correlation function is determined with the help of the quantity $c(r;t,0)c(0;t,0)$, which gives the correlation between the mobility of two particles separated by a distance r at two different instances of time 1.7.

$$G_4(r;t) = \langle c(r;t,0)c(0;t,0)\rangle - \langle c(r;t,0)\rangle^2 \tag{1.7}$$

here, $G_4(r;t)$ is known as the dynamic four-point correlation function because it measures the correlation of motion at two time points 0 to t, but spatially separated at 0 and r. This definition of the space-time correlation function is considered an important advancement in the characterization of dynamic heterogeneity. This suggests the existence of a critical length scale ξ_4, such that the correlation function $G_4(r;t)$ decays as:

$$G_4(r;t) \approx A(t)[exp(-r/\eta_4(t))]/r^p \tag{1.8}$$

where p is the critical exponent. The dynamic susceptibility ($\chi_4(t)$) can therefore be represented in terms of the correlation function as:

$$\chi_4(t) = \int d^d r G_4(r;t) \tag{1.9}$$

The $\chi_4(t)$ can also be obtained from the fluctuations in total mobility $C(t,0) = \int d^d rc(r;t,0)$, as:

$$\chi_4(t) = N[\left\langle C(t,0)^2\right\rangle - \langle C(t,0)\rangle^2] \tag{1.10}$$

The above formula is an effective measure of dynamic heterogeneity for all spatially and temporally separable systems and has become a central tool in characterizing the dynamic heterogeneity in glass-forming systems. The increase in the peak of $\chi_4(t)$ corresponds to a growing length scale ξ which has been found in various simulations. Therefore, the study of $\chi_4(t)$ and its associated growing length scale ξ provides useful information about the relaxation dynamics. Also, the growth of ξ suggests that the glass transition phenomenon is accompanied by a growing length scale and time scale [58]. Molecular dynamics simulations have also shown that the dynamic heterogeneity is associated with a short-ranged and medium-ranged structural order which is dependent on the glassy system chosen to study [59].

1.6 Theoretical developments

Some evidences show that the dynamic heterogeneity is associated with a structural component underlying the dynamic susceptibility, [60, 61, 62] but the possible link between the local structure and the dynamic heterogeneity and detailed experimental studies on systems showing dynamic heterogeneities is still lacking. In this context, several theories have been proposed to develop a framework for this dynamical behavior like the presence of cooperatively rearranging regions (CRRs), dynamic lengthscales, and timescales.

1.6.1 Adam Gibbs Theory (AGT)

In 1965, Adam and Gibbs developed a theoretical model explaining the relaxation behavior of glass-forming liquids. The AGT was a molecular kinetic theory that aimed to explain that the relaxation behavior of glass-forming liquids is dependent on the temperature and the temperature dependence of the relaxing liquids can be given by the exponential Arrhenius relation (Equation 1.1) [40]. They predicted that the glass-forming liquid requires activation energy for its relaxation which is independent of the temperature [40]. Further, they also predicted that the temperature-dependent relaxation times can be determined with the help of transition probabilities which they defined as cooperatively rearranging regions (CRRs). These CRRs are also variable and dependent on the temperature. According to AGT the CRRs are a subsystem of the glass-forming liquid and provided sufficient fluctuation, they are capable of rearranging themselves from one configuration to another and the size of these CRRs can be determined based on configurational entropy (Equation 1.3) [40, 42]. The AGT was a successful attempt to correlate the kinetic properties of the glass-forming liquids in terms of a thermodynamic framework but the experimental evidence in support of the theory was limited up to a certain temperature. Therefore, more theoretical models were developed to predict the dynamic behavior of glass-forming materials.

1.6.2 Mode coupling theory (MCT)

The Mode Coupling theory (MCT) was the first theoretical attempt to explain the dynamical behavior of the glassy system which was introduced in 1984. It is a purely first principle-based route towards the understanding of glassy behavior [63]. MCT aimed to predict the full microscopic behavior of glassy dynamics using the knowledge of static time-independent properties. It began with the prediction of microscopic behavior based on the static structure factor S(q) (Equation 1.4) as a series of temperatures or densities, but it failed to predict the behavior at temperatures lower than the mode coupling transition temperature (T_c) which is higher than the T_g. Later, the theory defined the self-intermediate scattering function F(q,t) (Equation 1.6), which predicted a two-step relaxation of the density-density correlation function. So far, MCT is the only theory that can predict the two-step stretched exponential relaxations. In extension to this, the MCT helped to understand the dynamic heterogeneities in the form of four-point dynamic susceptibility $\chi_4(t)$ (Equation 1.9). It correctly predicted the overall nature of correlation function $G_4(r;t)$ (Equation 1.7) indicated that the peak appearing in $G_4(r;t)$ is the signature of α relaxations and the peak will appear at a time scale close to α relaxation time. Another prediction of MCT is that the peak of $\chi_4(t)$ will diverge with temperature upon supercooling. The divergence of $\chi_4(t)$ is still debatable, some simulations and experiments have failed in this prediction but there is evidence of a power law growth of the peak height of $\chi_4(t)$ with decreasing temperatures in moderately supercooled liquids. An extension to MCT, also predicts the growth of dynamical correlation length ξ upon supercooling popularly known as Inhomogeneous Mode Coupling theory (IMCT) [64].

Even though MCT was successful in predicting the dynamical behavior of glasses, the application of MCT in simulations and experiments was quite critical. A major drawback of MCT was that the predicted transition temperature T_c was quite higher than the actual experimental glass transition temperature. Therefore, the overall predictions of MCT were only valid for a moderately supercooled liquid [65].

1.6.3 Random first-order transition (RFOT) theory

The Random first-order transition (RFOT) theory has become more popular over the past few years because of its successful prediction of the dynamic transition temperature, which was the basis of the failure of MCT. Along with the glass transition, RFOT also consistently predicts the nonequilibrium phenomenon of a glassy state based on the features of the free energy landscape for structural / configurational rearrangements at the microscopic scale [66]. According to RFOT, when the glass-forming liquid comes from high temperatures towards T_g, the dynamics slow down because of the presence of metastable states. The thermodynamic behavior is therefore controlled by these large number of metastable states which are similar to one another and would result in configurational entropy (S_c). On decreasing the temperature further beyond the transition temperature, the dynamics become an activated process where the particle has to cross a thermally activated barrier from one metastable state to another. According to RFOT, this activated process displays a relationship between the dynamical correlation length scales and time scales. Another important prediction of RFOT is that on extrapolating the S_c at lower temperatures, there comes a point at temperature T_K (Kauzmann temperature) where the entropy vanishes, and this point is predicted to be the thermodynamic transition temperature. It also predicts that in a temperature range $T_K<T<T_c$, the system fragments itself into mosaic states with a correlation length scale ξ. Therefore, the RFOT predicts that the dynamic heterogeneity is a mosaic of CRRs in a free energy landscape of a glass-forming liquid.

The RFOT has been successful in the prediction of the glassy dynamics in many glass formers experimentally and also in numerical simulations but it is still uncertain that the theory is valid for all glass formers [67, 68, 69, 70]. A clear understanding of the mutual relationship between static and dynamic length scales is still lacking. The presence of structural ordering is also not universal for all glass formers. Despite several drawbacks, the RFOT is the most preferable theory which has the most acceptable explanation of the dynamical behavior in glasses. The field is therefore open for the development of new models, simulations, and experimental works which can have a systematic and precise understanding of the glassy dynamics.

1.7 Significance of Glassy Polymers

As mentioned before, glasses are ubiquitous in nature and they can be found in a wide range of materials from metallic glasses to polymers, colloids, semiconductors, proteins, etc. An important characteristic of polymers that makes them a preferable candidate to study glassy dynamics is that the stereo-irregularity and sluggish dynamics of polymers make them hard to crystallize. Polymers are inherently amorphous, even crystalline polymers have as high as 60 % of crystalline domains. This characteristic makes polymer easier to form a glass. A popular method to form glass from the polymer is rapid cooling or quenching which leads to a higher prevalence of glass formation avoiding crystallization. This characteristic also makes glass polymer highly industrially relevant for a wide range of applications.

Over decades, the use of polymer has been extended in our day-to-day life, ranging from gas separation to corrosion-resistant coatings to drug delivery systems [71, 72, 73]. With the development of technology, the glassy state of polymers is an important concern to developing devices with improved performance because studies have shown that properties like the non-periodic order of glassy system help in increasing the overall conductance and transport characteristics. The glassy and rubbery state of polymers has also been beneficial in the development of biosensors, neutron detectors, and membranes for gas separation[71, 72, 74].

Although all glass formers have some salient features as discussed in the previous sections, the study of polymer glasses manifests slight differences due to the presence of long chain connectivity (due to inter and intra-chain interactions) and existence of several configurational states. The chain connectivity alters the nature of the flow during deformation. At the plastic yielding for polymers, the polymers have been driven into the glassy state [4]. When the polymer chains are entangled, they undergo plastic flow also known as ductile yielding where the material deforms irreversibly [11, 12]. Recently, there have been a lot of advances in the understanding of how chain dynamics affect the nature of flow during subsequent strain hardening and the viscoelastic properties of polymer dynamics near T_g [14, 15]. Along with the chain dynamics, the chemical structure of polymers also plays an important role in determining the mechanical properties of the polymer because packing and jamming of inter-chain segments dominate the intra-chain connectivity, thereby affecting the polymer deformation [17]. Therefore, the study of deformation in polymer glasses, leading to non-equilibrium dynamics of physical parameters, has several open questions which need to be explored.

Dynamical slowing down of relaxation dynamics affects not only the mechanical properties but also other macroscopic properties like a dielectric response, crucial for device performance especially in charge storage applications [75]. Moreover, with the widespread use of non-biodegradable polymers like polyethylene which is an environmental hazard, it has become important to look for alternatives that can be environment friendly.

1.8 Recent advances in Glassy systems

The anomalous properties of glassy systems on approaching the T_g have widely been studied and are continuing to be a field of interest for research in the current scenario due to wide applications of glassy materials, as discussed in previous sections. Despite numerous applications of glassy systems, the fundamental understanding of glassy dynamics has not been completely achieved. Recently, many theories, simulations, and experiments have been performed to address the fundamental questions of glassy physics. An important development is the observation of short to medium-ranged cooperatively rearranging regions in colloidal glasses. The molecular dynamics simulations have successfully determined the medium to short-range cooperative regions in a colloidal glass [59]. After this work, the presence of cooperatively rearranging regions has also been found in various other glass former like spin glasses [76], polymeric glass [77] and also in active matter and biological systems [70]. The CRRs significantly indicate the heterogeneity in the glassy dynamics. Recent atomistic simulations for polymer nanocomposites have shown a wide range of relaxation times which depends on the deformation rate and the presence of mechanical heterogeneity [78].

The presence of dynamic heterogeneities observed in simulations has led to the understanding of dynamic length scales and time scales in the glassy system. Dynamic mechanical analysis of polystyrene films has witnessed the presence of varying length scales from nanometers to micrometers in the glassy state of the polymer. This dynamical behavior is also accompanied by the enhanced mobility in the glassy polymer [79]. The mobility in polymer glass is proven to be dependent on the thickness of the polymer film [79] and the molecular mass of the polymer [80] not only for polystyrene but also for other polymers like poly(n-butyl methacrylate), polylactic acid, etc [80, 81]. It has also been experimentally observed that the relaxations in glassy polystyrene are different for bulk and film state of the polymer [79]. The molecular mobility in glassy materials also provides information about the physical aging of the material. A detailed experimental characterization of molecular mobility in microporous polymer films has presented local fluctuations of pores with several relaxation processes and a Maxwell-Wagner-Sillars polarization effect during the physical aging of the polymer [82]. Non-equilibrium scaling laws have recently been developed based on Mode coupling theory to demonstrate the physical aging and equilibration dynamics in glassy materials which says that the structural relaxation time is dependent on the depth of quench where the glass former shows a transition from simple aging to subaging and hyperaging states on going deeper into the glassy state [83].

Physical aging has also been found to have a critical impact on the macroscopic properties of glass formers. The study of mechanical properties of Poly-lactic acid has shown that the molecular mobility and reorientation of the polymer chains not only enhance the toughness and strength of the polymer but it also hinders the physical aging process [81]. The molecular interactions have also been studied and they are found to correlate with the adhesive force of a polymer film [84]. Therefore, the recent developments in glassy systems are aiming not only toward the fundamental understanding of the field but also at its effect on the applications of the glass formers. Despite numerous studies and discoveries, a complete understanding of glassy systems is still not achieved, requiring more experimental studies.

1.9 Motivation

Disordered systems like polymers, gels, and other glass former have become an inevitable part of our day-to-day life from plastic bags to insulating devices, from drug delivery to scaffolds, and many more. Unveiling the behavior of disordered systems has always been an important concern for decades because anomalous dynamics like structural relaxation and cooperatively rearranging regions at the microscopic scale have been found to control the macroscopic properties like the dielectric and mechanical response of the system. Heterogeneous plastic deformation, as well as physical aging, has a microscopic origin. Therefore, from the fundamental point, it becomes of immediate concern to answer some major unresolved questions about glasses: What is the origin of the dynamic slowdown in glasses? Does it have a molecular origin? Does the glassy dynamics have a structural correlation? and last but not least are these properties universal for all glass formers? Simulations have shown that the glassy dynamics is governed by molecular scale mobilities which can affect the mechanical response of the material [14, 15]. Despite years of research to understand the origin of the glassy dynamics in the 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 a disordered system, i.e., polymers near their glass transition temperature. The anomalous properties of glasses close to T_g, like the dynamic slowdown, physical aging, etc. not only draws attention to understanding their overall behavior but it also raises a concern for perspective applications of the material.

The intriguing applications of glassy polymers ranging from gas separation to corrosion-resistant coatings to drug delivery systems are due to their disordered nature which leads to increased conductivity, permeability and mechanical resistance [71, 72, 73]. As discussed in the previous section, the macroscopic properties of polymers tend to divert from their equilibrium behavior near T_g which can be beneficial to polymer applications. According to a recent study by Zheng Chen, et. al. the thermally responsive polymer near glass transition can become a suitable candidate for switching devices as they experience a high and instant drop in conductivity on reaching T_g which can be useful in building safe batteries with self-regulating mechanism [85]. Most applications use non-biodegradable polymers which are a major source of environmental pollution. The need of the hour is to develop methods to replace more environmentally friendly biodegradable polymers in place of non-biodegradable polymers. This necessitates a comparative structure-property analysis of biodegradable polymers with respect to polyethylene.

1.10 Objectives

For a better understanding of glassy dynamics based on experimental evidence and to bridge the gap between the fundamental processes and the application of glassy polymers, the present study aims to fulfill the following objectives :

1. Comparison of the 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.

The work presented in this thesis addresses these issues with the help of experimental studies on biodegradable as well as nonbiodegradable polymers at the molecular scale, micro-scale, and macroscopic scale.

1.11 Thesis outline

The chapters in the thesis address the aforementioned objectives, and the results obtained are summarized as follows :

- **Chapter 2**: In Chapter 2, the response to mechanical and thermal perturbations is compared for a biodegradable polymer with a non-biodegradable polymer with the help of tensile testing and Raman scattering experiments. 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 indicating that molecular mobility is an important parameter that influences the macroscopic mechanical properties.
- **Chapter 3**: Chapter 3 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. These responses to these thermal cycles reveal a cooperative motion of molecular motion in the main chain as well as the side branch of the polymer. The slow thermal perturbation provides evidence of the deviation of relaxation dynamics from Arrhenius behavior on crossing T_g.

- **Chapter 4**: Chapter 4 continues the study of Chapter 3 with evidence of the presence of a mosaic of cooperative regions with different molecular conformational domains and dynamic heterogeneity. We have attempted to obtain a spatial and temporal correlation within the heterogeneous domains and have successfully determined the experimental dynamic susceptibility from Raman mode intensities.

- **Chapter 5**: Chapter 5 focuses on the application part, which aims to the development of polymer composite with tunable mechanical properties and a methodology development to study the micro-mechanical properties via diffusion dynamics using Fluorescence Recovery after Photobleaching (FRAP) experiments.

- **Chapter 6**: Chapter 6 concludes the thesis providing future perspectives to the work.

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