Abstract

Disordered materials are ubiquitous in our day to day life in the form of polymers, emulsions, colloids, gels or liquids. The importance of disordered systems lies in their anomalous properties ranging from solid like behavior to fluid like behavior under various conditions and perturbations. Despite years of theoretical, simulations or experimental research, there are still many questions unanswered in the field of disordered materials, especially glassy systems. Understanding the origin of glassy behavior, which is marked by the presence of dynamic heterogeneities, dynamic slow-down and cooperatively rearranging regions on approaching the glass transition temperature has been the aim of several groups worldwide. The dynamical behavior of the disordered materials also influences the macroscopic properties of the material which impacts the applications of the material. Not only this, it is important to study the disordered materials at the microscopic and molecular scales also in order to understand overall behavior of the material for better applicability. The present thesis aims to understand the glassy behavior of polymers at the molecular level and its impact on the macroscopic properties.

The molecular scale vibrational properties of a biodegradable polymer, polypropylene carbonate, were compared with a non biodegradable polymer, polyethylene using Raman spectroscopy. Thermal perturbation was used to drive the system out of its equilibrium state. Impact of thermal quench and ramp on molecular scale mobility was reflected in the variation of FWHM of the Raman peaks. Moreover, molecular mobilities were observed to evolve with time after thermal perturbation. A correlation between the macroscopic mechanical properties of the polymers with the vibrational Raman characteristics was observed, which established that the molecular motion can affect the macroscopic properties. Molecular mobility and glassy behavior was studied using Raman spectroscopy for polyvinyl acetate (PVAc), a non-biodegredable polymer, which has glass transition temperature near room temperature. A strong evidence of the presence of heterogeneous molecular mobility was observed, which was found to be dependent on the temperature and time after thermal perturbations. Molecular relaxation dynamics was observed to deviate from caging dynamics to cooperative dynamics on crossing the glass transition temperature. A strong correlation among the Raman vibrational modes was observed, which indicated the presence of cooperativity between the polymer main chain and side branches. A 2-D mapping of the polymer film using Raman spectroscopy showed the presence of cooperatively rearranging regions as a function of time after thermal perturbation. Heterogeneous domains with variable Raman intensity were observed which provides an evidence of the presence of dynamic heterogeneities at the molecular scale of the polymer. The dynamic heterogeneities also show cooperativity between the dynamically relaxing domains. In order to study the micro-scale dynamics of mechanical properties of polymer solutions, a methodology was developed using Fluorescence Recovery after Photobleaching (FRAP) technique. This was applied to study the micro-scale mechanical properties of polyethylene glycol solution in absence and in presence of nanofillers - bentonite clay and carboxymethyl cellulose (CMC). The effect of polymer and nanofiller concentration was observed in the diffusion coefficient values obtained from FRAP experiments. The addition of bentonite led to aggregation which introduced micro-scale heterogeneities in the structure. This solution structuring was studied at three length scales, using microscopy and small angle scattering studies. Diffusion coefficient values were found to be very sensitive to the presence of micro-scale inhomogeneities present in the material. The detection of these micro-scale inhomogeneities is important as it can affect the mechanical properties of the material at the macro-scale also.

Overall, the present study is an experimental attempt to not only answer the fundamental questions of glassy physics but also to develop a strong correlation between the molecular scale, micro-scale and macroscopic properties of polymers which can be useful for better applicability of the material.