Abstract

Polymer-small particle multicomponent colloidal suspensions are an important class of soft matter that is encountered in several industries such as agriculture, pharmaceutical, food, paints, ink, coating etc. The mechanistic origins of several of their macroscopic properties can be traced back to the intricate interactions occurring at colloidal length scales. Among various small particles, clay and carbonaceous (such as graphene, graphene oxide, and carbon nanotubes) are of special interest due to potential applications of these systems in coating, paints, polymer nanocomposites etc. Colloidal states of such multicomponent systems depend on several factors, a few of which are: particle/polymer concentration, salt concentration, pH, temperature etc. In this thesis, we have studied clay and graphene oxide suspensions with and without polymer to explore their various colloidal interactions. We use different experimental and computational tools for studying various aspects of these suspensions. Rheology is primarily used to investigate the macroscopic flow behavior of these suspensions. For investigation of mesoscale assembles, we use small angle x-ray and neutron scattering. We use dielectric relaxation spectroscopy for relaxation behavior of these suspensions. Finally, zeta potential measurements are used to investigate the stability of these suspensions. In certain cases, we have also used coarse-grained molecular simulations to investigate the polymer chain-particle interface formed.

In the first chapter, we investigate poly(vinyl alcohol)-laponite multicomponent systems. The effect of concentration of adsorbing polymer on the aging dynamics of laponite suspension is studied by oscillatory shear rheology. We observe that specific concentration of adsorbing polymer strictly regulates the aging dynamics of laponite-PVOH multicomponent systems. The observed aging pattern is analyzed by dividing it into three sub-regimes, across which the suspension's elastic modulus showed an oscillatory relationship with polymer concentration. A mechanism to explain this phenomenon is developed after getting shreds of evidence from complementary tests. These are a) small angle neutron scattering b) structure recovery upon shear melting c) zeta potential estimation. Colloidal stability of suspensions in all sub-regimes during the timescale of measurement is also analyzed by invoking both DLVO and non-DLVO theories. The observation and analysis highlight the effect of concentration of adsorbing polymer on aging clay suspensions and have direct applications in stabilization, rheology modification, as well as polymer nanocomposite preparation.

Secondly, an anomalous temperature-viscosity relationship in organoclay/polymer multicomponent system is explored. Suspension of hydroxyl-terminated polybutadiene (HTPB) and montmorillonite are studied. In this study, the formation of polymer-particle microstructure at various concentration of clays as a function of temperature and flow field is observed. Suspension shows a transition from liquid rich behavior to solid rich type behavior due to the formation of microstructure at higher clay loading, and an anti-Arrhenius behavior is observed for HTPB-Cloisite10A multicomponent suspension. To quantify the microscopic structures and interactions, small angle x-ray scattering (SAXS) and dielectric relaxation spectroscopy are conducted at different temperatures. A collective interpretation of rheology, SAXS, and dielectric relaxation results are used to reach an explanation for the anti-Arrhenian viscosity-temperature relation.

Thirdly, polymer-graphene oxide multicomponent suspensions are investigated. In this work, small angle neutron scattering (SANS) is used to directly measure the thickness of adsorbed polymer layer onto the surface of 2-D graphene oxide sheets. In order to fit the scattering traces from GO suspension, two models namely, flat cylinder (for single 2-D sheets) and cylinder (for aggregated sheets) are employed using sasfit software. To estimate adsorbed polymer thickness on GO sheet, scattered intensities from suspension are fitted using core-shell cylinder and thick cylindrical models. It is found that adsorbed polymer layer thickness (δ) scales with the radius of gyration (R_g) of the polymer as $\delta = R_g^{0.24}$. Further, coarse-grained simulations were used to test the observed experimental trends.

Lastly, the colloidal interactions in aqueous suspensions containing a dispersion of laponite and graphene oxide are explored. The high colloidal stability of these suspensions are analyzed by estimating net interaction potential energy. Evolution of modulli of laponite-GO suspension as a function of GO concentration is monitored by employing rheological studies. Further, SAXS experiments are carried out in order to a have deeper insight into shape and microstructure formation between laponite and GO particle.

The work described in this thesis finds applications in the paint, coating, paper, cosmetic industry etc. as well as in drilling fluids, where flow behavior of suspensions is of substantial importance.

Keywords: Polymer-nanoparticle suspensions, flow behavior, aging, stability, adsorption.