CHAPTER IX
CONCLUSIONS AND RECOMMENDATIONS

In this study, polyaniline (PANI) was synthesized via oxidative coupling polymerization in acid conditions and its conductivity was controlled by doping in camphorsulfonic acid (CSA) solution and de-doping in solution of ammonia. The suspension of un-doped PANI/silicone oil suspensions were then prepared and their electrorheological (ER) properties were investigated in oscillatory and steady shear as functions of electric field strength, particle concentration, host fluid viscosity, and operating temperature. We also studied an electroviscoelastic behavior of camphorsulfonic acid (CSA) – doped polyaniline (PANI) particles embedded in an elastic cross-linked PDMS matrix

9.1 Electrorheological Properties of Polyaniline Suspensions: Field-Induced Liquid to Solid Transition and Residual Structure

When the ER properties of PANI/silicone oil suspensions were investigated with respect to the effect of electric field strength, particle concentration, and silicone oil viscosity on dynamic shear moduli, G' and G" and yield stress, τ_y. Consistent with previous observations, the magnitude of the ER response is enhanced with increasing electric field strength and particle concentration. The dynamic moduli, G' and G" increase dramatically, by 5 orders of magnitude, as the electric field strength is increased to 2 kV/mm. A viscoelastic liquid to solid transition occurs at a critical electric field strength, in the range E_c = 50-200 V/mm, whose value increases with particle concentration and decreases with host fluid viscosity. The fibrillar structure formed in the presence of the applied field has a static yield strength τ_y, whose value scales with electric field strength as $\tau_y \sim E^{1.88}$. When the field is switched off a residual structure remains, whose yield stress increases with the strength of the applied field and particle concentration. When the applied stress exceeds the yield stress of the residual structure, fast, fully reversible switching of the ER response is obtained.

9.2 Critical Electric Field Strength for Liquid to Solid Transition of Polyaniline/Silicone Oil Suspensions

Polyaniline (PANI) was synthesized via oxidative coupling polymerization in acid conditions and de-doped in ammonia solution. The electrorheological (ER) properties of the PANI/silicone oil suspensions were investigated in oscillatory shear, with particular focus on the high frequency region where a crossover in G'(ω) and G"(ω) signals the onset of a dissipative relaxation process, associated with motion of PANI partciels within the fibrillar structures generated by the electric field.. The relationship between the crossover frequency, ω_c, and the electric field strength (E) was investigated as a function of matrix viscosity and shear strain.. We find that ω_c increases with increase in field strength, and decreases with increase of matrix viscosity and strain amplitude, in qualitative agreement with a theoretical model which relates the relaxation mechanism to the competition between hydrodynamic and electrostatic forces between PANI particles within thick fibrillar structures. at the crossover point, the critical dimensionless parameter, the Mason number (Mn), varies with Peclet number (Pe) according to a scaling relation $Mn \sim Pe^{0.091}$.

9.3 Hysteresis and strain hardening in the creep response of a polyaniline fluid

The electrorheological creep response of PANI)/silicone oil suspensions near the yield point is investigated using parallel plate rheometry. Controlled-stress, thixotropic loop experiments exhibit a pronounced hysteresis, from which we determined the static yield stress ($\sigma_{y(static)}$), as the stress where onset of flow occurs on the upward part of the loop, and a dynamic yield stress ($\sigma_{y(dynamic)}$), defined as the stress at which flow ceases on the downward part of the loop. The magnitude of the hysteresis, as characterized by the area under the loop, increases substantially with applied field strength and particle concentration, but decreases with increase of temperature. Consistent with literature data, the creep compliance shows an evolution from viscoelastic to viscoplastic to viscous flow behavior as the applied stress increases through the yield point. In the viscoplastic regime, the apparent

equilibrium compliance, J_e^{app}, shows a discrete pre-yield transition to higher values, indicating a seemingly-enhanced ductility as the applied stress nears the yield point. Measurement of the static yield stress following these creep experiments suggests that the origin of this transition is a pronounced strain-hardening effect. We conclude that strain-hardening contributes to the hysteresis observed in the thixotropic loop test.

9.4 Strain-hardening in the oscillatory shear deformation of a polyaniline electrorheological fluid

An electrorhological (ER) fluid, consisting of polydisperse polyaniline (PANI) particles, having irregular shapes, dispersed in a silicone oil, was subjected to cyclic strain annealing treatments under an external electric field, involving application of oscillatory shear (strain γ = 1%, deformation frequency ω = 1 rad/s) for sequential time periods of increasing duration, during which the storage and loss moduli were monitored. After each annealing period, the sample was subjected to a controlled strain sweep, to determine the yield stress, and erase the ER structure. During each annealing period, the storage modulus was observed to increase, and the loss modulus to decrease, each eventually approaching an asymptotic constant value. The yield stress was also observed to increase following each annealing period. These observations seem consistent with literature reports of shear-enhanced yield stress in a model ER fluid using sequential creep-recovery cycles. After three annealing cycles, a gradual decrease in the initial storage modulus, following each prior strain sweep was observed, apparently reflecting some irreversible change in ER properties (e.g. agglomeration and sedimentation of the marginally-stable PANI particles).

9.5 Electromechanical Response of a Soft and Flexible Actuator Based on a Cross-Linked Poly(dimethyl siloxane) Network

Composites films, consisting of camphorsulfonic acid (CSA) – doped polyaniline (PANI) particles dispersed in poly (dimethyl siloxane) (PDMS) networks

were prepared and their electroviscoelastic behavior investigated as a function of electric field strength, particle concentration, and operating temperature. The storage modulus G' increases by an amount $\Delta G' \sim$ 10-50%, depending on PANI volume fraction, when the applied field strength is increased to 2 kV/mm. This increase in modulus is only partially reversible (about 37.5% recovery) on the removal of the applied field. The magnitude of $\Delta G'$ increases with increasing particle content: $\Delta G'$ = 417 Pa at a 2 % vol and increases to 26,243 Pa at a 20 % vol. The temperature dependence of $\Delta G''$ shows a maximum at $T \sim 325\ ^{o}K$, where the temperature-dependent conductivity of PANI also exhibits a maximum value. We report the electromechanical response of a free standing PANI/PDMS composite film, containing 10 vol% PANI particles, when suspended in silicone oil between two flat parallel copper electrodes. When subjected to an electric field, the film exhibits a deflection, whose magnitude increases with increasing electric field strength, but decreases slightly when the particle concentration is increased to 20 vol%. The origin of the electromechanical response apparently resides in the conductivity-controlled polarization of the doped PANI, since the undoped PANI has negligible electromechanical effect.

9.5 Recommendations for future work

The ER properties of polyaniline/PDMS composites in both oscillatory and steady shear flow have been investigated in this work. Some important parameters, for examples dielectric properties of this suspension, presenting of surfactant are interesting for further investigation to provide clarification and more understanding in the ER fundamentals. The relative polarizability of the system which governs the ER response is the one parameter that needs to be studied. In the dimensionless parameter study, extending the operating temperature to the wider range would provide useful data that is applicable to predict ER behaviors of the suspensions in various practical conditions.