

Rheology and microstructure of fumed, colloidal particles suspended in isotropic and anisotropic media: Role of particle shape, surface chemistry and applied external fields

Abstract

The fundamental understanding of the behaviour of particulate suspensions in isotropic and anisotropic dispersing media is of critical importance for applications pertaining to hydraulics, robotic, microfluidic, sensory and display devices. While the isotropic silicone oil enables instantaneous polarization of electrically polarizable particles to form chain-like structures in the direction of an electric field (E), incorporation of particles in an ordered matrix of anisotropic liquid crystals (LCs) leads to the generation of different self-assembled structures. The present thesis systematically investigates the interplay of different factors controlling the rheology, structure and phase behaviour of suspensions. Two types of dispersing media are explored in this work: 1) the isotropic silicone oil and 2) Nematic LCs (NLCs) having rod-like molecules with only orientational order.

The first aim of the thesis is to understand the effect of addition of fumed alumina (Al_2O_3) nanoparticles (primary particle size ~ 21 nm) in silicone oil medium on the rheology, electrorheology and structure of Al_2O_3 /silicone oil suspensions. Our results demonstrate that in the absence of E, the suspensions form gels at and above the nanoparticle loading of 10 wt%, resulting in plateau of G' (storage modulus) at the low angular frequency (ω). We further show that these suspensions are extremely sensitive to the pre-shearing history and exhibit thixotropic behaviour, exemplified by the transient step-down in shear rate experiments. When the 0.5 wt% - 5 wt% Al_2O_3 /silicone oil suspensions are subjected to an external $E = 0.25 - 2$ kV/mm, a transition from liquid-like to solid-like behavior occurs, marked by diverging low shear viscosity, frequency independent G' and appearance of yield stress. Moreover, our results suggest that the above the threshold $E = 0.5$ kV/mm, the suspension electrorheological (ER) response is not dependent on the applied pre-shear and

the relative viscosity does not follow the $\frac{\dot{\gamma}}{E^2}$ scaling ($\dot{\gamma}$: shear rate) based on the polarization force model.

We next investigate the implication of using elongated Goethite (α -FeOOH, length (l) = 488 ± 20 nm, aspect ratio = 5 ± 0.8) particles in the same silicone oil medium on the rheology and microstructure of α -FeOOH/silicone oil suspensions at different E . Even at a low E of 0.25 kV/mm, the liquid-like suspensions with ϕ of 0.025 and 0.039 transform into solid-like gels, marked by ω independent G' and yield stress which varies with $E^{1.5}$, consistent with the conduction model framework. The optical microscopy demonstrates that the α -FeOOH particles dispersed in the silicone oil medium are capable of forming an electric field driven network under equilibrium conditions of no shear.

We now present a completely different perspective by replacing the isotropic silicone oil with the anisotropic NLC medium, N-(4-methoxybenzylidene)-4-butylaniline (MBBA), for dispersing fumed Al_2O_3 nanoparticles. The suspensions with nanoparticle $\phi \geq 0.014$ form solid-like self-supporting gels with $G' > 10^3$ Pa and follow the soft glassy rheology (SGR) model, described by $G' \sim \omega^{(x-1)}$ scaling, where x is the effective noise temperature representing the structural disorder in suspensions. We also show that unlike fumed Al_2O_3 /silicone oil suspensions, fumed Al_2O_3 /MBBA suspensions can recover 60% of the original structure even after the application of large amplitude oscillatory strain (γ). The optical microscopy coupled with the differential scanning calorimetry (DSC) reveal that fumed Al_2O_3 nanoparticles cause a significant depression in the nematic-isotropic transition temperature (T_{NI}) relative to the particle-free MBBA, due to the quenched random disorder (QRD) resulting from the confinement of NLC in the network of nanoparticles. We further demonstrate that the reversible E -driven phase transition occurs only at and above a critical nanoparticle ϕ of 0.005.

The next aim of the thesis is to systematically study the role of particle surface chemistry on the rheology and structure of suspensions of fumed and colloidal silica particles in the NLC, 4-cyano-4-pentylbiphenyl (5CB). We show that the suspensions of hydrophilic fumed and colloidal particles in 5CB undergo sol to gel transformation at a lower particle ϕ than the hydrophobic fumed and colloidal silica particles. Moreover, the hydrophilic silica/5CB suspensions exhibit SGR characteristics while the hydrophobic particles-in-5CB

suspensions show the features of flocculated gels. We show that below T_{NI} , the NLC domains get restricted in the existing network of fumed hydrophilic silica particles, leading to confinement and subsequently, SGR characteristics. In contrast, the well dispersed hydrophobic fumed silica in 5CB gets expelled at the isotropic-nematic interface during phase transition to form a network. We believe that the observed rheological response and underlying microstructure is due to different anchoring of 5CB molecules on the surface of silica particles.

In conclusion, our work has demonstrated the capability of fumed Al_2O_3 /silicone oil and FeOOH/silicone oil suspensions to serve a positive ER response system. On the other hand, dispersing fumed Al_2O_3 nanoparticles in the NLC paves a way to produce structurally disordered particles-in-NLC suspensions which can respond to an external E. We also show that depending on the particle surface chemistry and the NLC anchoring on the particle surface, the suspensions rheology can be tuned. To summarize, our work illustrates how the behaviour of suspensions can be engineered as a function of dispersing medium, particle loading, shape, surface chemistry and external E to provide a basis for various applications pertaining to sensing, display, E-driven phase changing and temperature measuring devices.