Structure, Rheology, and Electrical Conductivity of High-Structured Carbon Black Suspensions

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High-structured carbon blacks are commonly used as electrically conductive additives in electrode slurries that are either processed into solid electrodes for batteries and fuel cells or used as flowable electrodes for semi-solid flow batteries. For these slurries, it is necessary to predict and control the microstructure under various processing conditions to achieve the desired rheological and electrical properties. Although present in relatively small mass fractions, the hierarchical microstructure formed by the carbon black particles significantly affects the viscosity, conductivity, and stability of the slurry. Research on model suspensions of carbon black show many complex shear- and shear history-dependent properties that are associated with proposed microstructural changes, but few investigations directly measure or characterize the microstructure under flow. Thus, there is a scientific need to perform direct measurements of the microstructural origins of these complex behaviors, which have technological value for optimizing the formulation and processing of electrode slurries. To this end, the overarching goal of this dissertation is to develop, by experiment, such structure-property relationships between the rheological, electrical, and microstructural properties of carbon black suspensions under varying formulation, shear, and shear history conditions.

A significant contribution of this dissertation is the direct measurement of the shear-dependent microstructure of carbon black suspensions under varying formulation conditions and the subsequent rationalization of the resulting structure-property observations using dimensionless groups. These novel structure-property measurements were performed *in situ* using simultaneous rheological and small angle neutron scattering (Rheo-SANS and Rheo-USANS) techniques, which allows for direct correlation of the rheological properties with the microstructure. As these measurements are the first systematic study of the shear-dependent microstructure in flocculated

suspensions, they address many long-standing hypotheses concerning the microstructural origin of many shear-induced behaviors such as apparent shear-thickening, shear-thinning, tunability of quiescent properties, and prolonged transient responses.

These measurements confirm that the reversibly thixotropic shear-thinning behavior observed in these suspensions arises due to the self-similar break up of carbon black agglomerates with increasing shear rate. For suspensions with varying chemistries and volume fractions, the agglomerate break up is found to depend on the dimensionless Mason number, which compares the cohesive force holding particles together in an agglomerate to the shear force driving particles apart. Additionally, many of the commonly observed, unexplained behaviors are linked to a measured dramatic, shear-induced structural transformation from large, dense agglomerates to small, open agglomerates at a critical shear condition. Spatiotemporally resolved measurements show that the formation of large, dense agglomerates leads to shear-induced sedimentation and a prolonged transient decrease in viscosity. This structural transition is predictable using the inverse Bingham number, which compares the measured stress to the yield stress of the suspension.

Importantly, this dissertation shows that the rheological and electrical properties of carbon black suspensions arise from different microstructural origins. By probing the electrical and mechanical percolation behavior, it is found that electrical percolation is coincident with a clustered fluid phase at low volume fractions and mechanical percolation arises due to formation of a system-spanning, stress-bearing network of jammed agglomerates. The effect of these disparate microstructural origins is observed under shear where with increasing shear rate, a shear-thinning viscosity is coupled with a suspension-specific increase or decrease in electrical conductivity. These findings have implications on the processing of carbon black suspensions as it is apparent that the electrical and rheological properties are independently tunable.