Title: Compatibility/incompatibility in surface-modified, aggregated, precipitated silica nanocomposites
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Time Span: Two years
Number of Graduate Students: 2

The dispersion of nano particles in viscous polymers is dictated by kinetics; interaction potentials between particles; and interfacial compatibility between the matrix and dispersed phases. It was previously proposed that an analogy can be made between thermally dispersed colloids and kinetically dispersed nano particles in viscous media for cases where only weak interactions exist between particles allowing for a mean field description under the Ginzburg criterion such as for carbon black dispersed in polybutadiene elastomer. For predominantly disordered systems the second virial coefficient modeled via the random phase approximation can be used to quantify the quality of dispersion;[1-3] additionally, the nano-scale network mesh size can be calculated, which is related to dynamic properties.[4] However, this approach fails for nano-particles with surface charges or other strong interactions that lead to somewhat correlated structures. We have recently proposed a methodology to extract the structural details for such systems using a modification of the Born-Green approximation that accounts for different domains of correlation due to varying accumulated strain, as opposed to the more traditional Percus-Yevick approximation that considers a single average mesh size.[5] A comparison of structural emergence in systems with weak and strong interactions is shown in Figure 1.
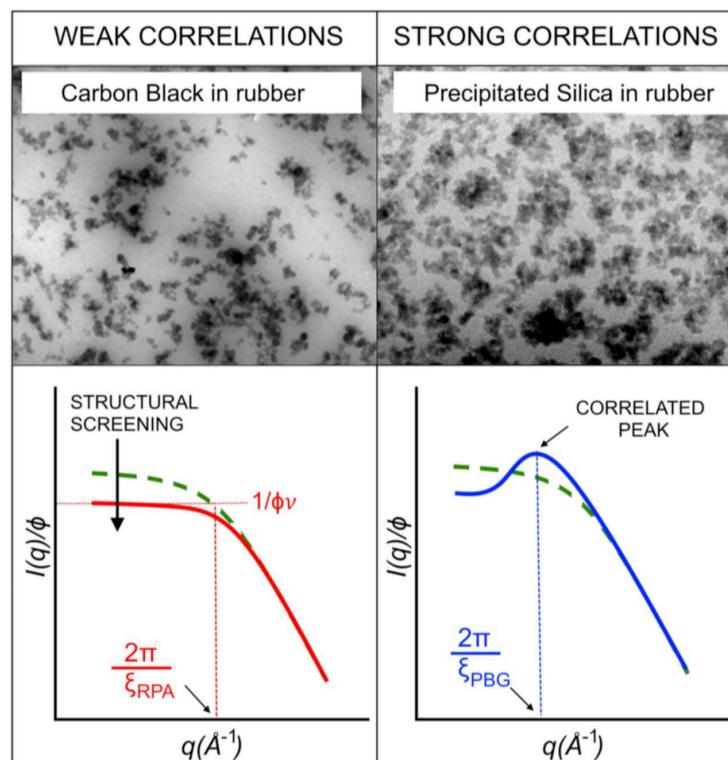

Figure 1. A schematic of the reduced scattering intensity as a function of reciprocal space vector for weakly and strongly correlated nanofillers along with TEM micrographs. The two micrographs are clearly distinct in nanoaggregate arrangement, randomly-dispersed for carbon black [4] and oriented/correlated for precipitated silica [6] in rubbers.

Many studies of dispersion largely involve model systems composed of spherical silica particles with variable surface treatments.[6] However, industrially relevant products often display a complex multi-level hierarchical, nano- to macro-scale structure. Control over this complex multi-hierarchical structure can be achieved through manipulation of filler-polymer compatibility/incompatibility such as by varying the silanol surface density, by chemically-tailoring the surface, and by grafting low molecular weight polymers. It is expected that these modifications can control dispersion and the associated emergent multi-hierarchy. From the mesh size and packing of an emergent network of aggregates, the state of dispersion and the interaction potential for coarse-grain simulations can be determined.

For this study, we propose to conduct ultra-small angle X-ray scattering measurements on untreated precipitated silicas, silicas with varying silanol density on the surface, silicas with silane treated surfaces and surface grafted silica in polystyrene, styrene-butadiene rubber and polydimethylsiloxane polymers with different molecular weights.

References:
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[2] Rishi, K. et al. A Thermal Model to Describe Kinetic Dispersion in Rubber Nanocomposites: The Effect of Mixing Time on Dispersion. Polymer 2019, **175**, 272–282.
[3] McGlasson, A. et al. The Effects of Staged Mixing on the Dispersion of Reinforcing Fillers in Elastomer Compounds. Polymer 2019, **181** (May), 121765.
[4] Rishi, K. et al. Impact of an Emergent Hierarchical Filler Network on Nanocomposite Dynamics. Macromolecules 2018, **51**, 7893–7904.
[5] McGlasson, A. et al. Quantification of dispersion in polymer nanocomposites for weakly and strongly correlated nanofillers. Macromolecules 2020, **53**, 2235–2248.
[6] Akcora, P. et al. Anisotropic self-assembly of spherical polymer-grafted nanoparticles. Nature materials 2009, **8**, 354-359.