Title: Hierarchical Emergence in Reinforced Elastomers.
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Number of Graduate Students/Post Docs: 2 GS
Time span: Two years
Budget: $400,000/2yr

Abstract:

Nanoparticles are necessary for normal use of elastomers since the tear strength and modulus for most elastomers is generally poor in the absence of aggregate filler networks. Nanoparticles also enhance the dynamic performance. The properties of these commercial nanocomposites are linked to the multi-hierarchical structure which emerges from carbon and/or silica nano-aggregates when milled with an elastomer in the presence of oil and other additives. Recent X-ray tomographs have shown the emergence of a micron- to millimeter-scale regenerative filler network which is responsible for high-strain mechanical response and recovery. The assembly of a micron-scale network from nanoparticles is controlled by processing geometry, concentration, surface conditions, accumulated strain, particle size and topology which impact the nano-dispersion and finally the assembly. We have recently developed a method to quantify nano-dispersion using X-ray scattering and the second-virial coefficient. The second virial coefficient can be used to calculate an interaction potential that can be used in DPD simulations to predict the emergence of filler networks. It is proposed to further develop this approach to understand the processing conditions that lead to optimal micron-scale network formation. The project will develop control over the emergent micron-scale filler network through correlation of the quantified nano-dispersion to emergence using experimental measurements and simulations.

Summary of Project:

The proposed approach builds upon our work on polymer-filler systems to quantify nano-scale dispersion, using ultra-small angle X-ray scattering, dielectric spectroscopy, oscillatory rheometry and coarse-grained dissipative dynamics simulations. [1-7] Figure 1 (a) shows the emergence of a micron scale network from nanoparticles in carbon black filled polybutadiene nanocomposites as a function of concentration. At low concentrations dispersed nanoaggregates are observed, above about 5% by volume these aggregates locally percolate into clusters, at about 20% by volume percolation of these clusters in a micron scale network occurs. The dispersion of nanoaggregates controls clustering which controls formation of the large-scale network. Figure 1 (b) shows the signature of these two percolations in X-ray scattering and in oscillatory rheology. The solid symbols are the storage modulus as a function of frequency. At high frequency the filled (black) and unfilled (red) elastomer can be scaled by the volume fraction following the Guth-Gold model. This is the filler displacement regime where filler structure is not a factor. At frequencies below $1/\tau^*$ the modulus is enhanced beyond the displacement law due to aggregate overlap. In scattering this point is found in scattering vector at the intercept of the screening from the filled sample with the dilute reduced scattering curve. This point reflects the size of the local network formed by percolated aggregates. At lower frequency the filled storage modulus (black filled squares) scales with the loss modulus (hollow squares) indicating a network of clustered aggregates at frequencies below $1/\tau^{cc}$ were a weak power-law of -2.2 is observed in scattering for a ramified network on the micron scale. The screening plateau at $1/(\phi_f \nu)$ in scattering can be used to determine the second virial coefficient and the interaction potential for filler particles, which can be used in coarse grain DPD simulations to predict the observed micron-network emergence.

It is often assumed that miscibility and compatibility of filler particles are important to the manufacture of enhanced property nanocomposites. However, the complicated multi-hierarchical structure shown in Figure 1 shows that controlled incompatibility that allows for the emergence of

locally percolated aggregate clusters that can then form a micron-scale network controls many of the properties.
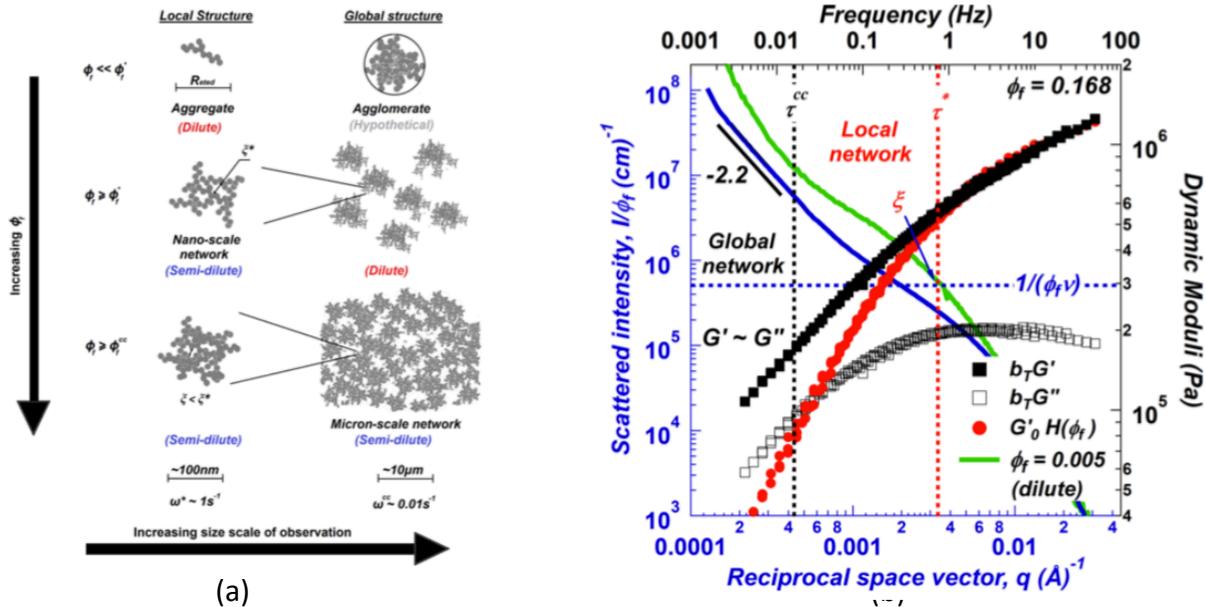

Figure 1. a) Sketch of structural hierarchies under dilute ($\phi_f < \phi_f^*$), nanoscale semi-dilute ($\phi_f^* \leq \phi_f \leq \phi_f^{cc}$), and micrometer-scale semi-dilute ($\phi_f \geq \phi_f^{cc}$) conditions and under distinct size/frequency scales of observation. The local percolation is associated with a nanoscale network, whereas global percolation is associated with a micrometer-scale network. [7] b) Graphic summarizing the hierarchical network model as supported by mechanical and structural data. Red circles are for the unfilled elastomer scaled storage modulus. Filled squares are for $\phi_f = 0.168$ filled sample storage modulus. Open black squares are the loss modulus for the filled elastomer. The blue line is the scattering curve for the filled sample, $\phi_f = 0.168$, in the semi-dilute regime, green line for $\phi_f = 0.005$ in the dilute regime. Top axis is frequency with dynamic moduli on the right axis; the bottom axis is the reciprocal space vector with left axis the scattered intensity. Two points link the top and bottom axes, τ^* to the right and τ_{cc} to the left.

The proposed approach builds upon our work on polymer-filler systems to quantify nano-scale dispersion, using ultra-small angle X-ray scattering, dielectric spectroscopy, oscillatory rheometry and coarse-grained dissipative dynamics simulations. The objective of these approaches is to accurately describe the connection between multi-hierarchical structures and properties at different frequency and size scales. Prediction of the formation of complex hierarchies requires computational techniques using analytic potentials and verified by empirical observations. One important goal is to link constraints at the mesoscale level (filler texture, surface area, primary particle size and surface functionalization) with aggregate structure.

Aims of Project:

1) Experimentally explore mixing geometry and time; surface functionality; aggregate topology and size; additives such as oil; polymer matrix on the nano-dispersion using the second-virial approach.

2) Relate the nano-dispersion and aggregate cluster morphology to the emergence of a micron-scale network.

3) Use the second virial coefficient to provide potentials for DPD simulations of network emergence.

4) Develop a predictive tool to design new emergent micron-scale networks.

5) Experimentally use simulation results to produce new reinforced elastomers with controlled properties.

Outcome of Work:

The project will result in a new understanding of structural emergence in reinforced elastomers. This will impact the design of complex elastomer nanocomposites.

References:

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