Title: In-situ crystallization kinetics study on dispersion in Polyethylene carbon black nanocomposites
PI: Greg Beaucage, Darrin Pochan
Time Span: Two years
Number of Graduate Students: 2

Commercial nanocomposites such as polyethylene (PE) pipes are fabricated from high carbon black loaded masterbatches that are blended with suitable carrier resins. A base resin with a higher viscosity than the masterbatch would inhibit filler incorporation whereas a lower viscosity base resin could lead to reduction in the crystalline content. Brittle failure in these systems due to filler agglomeration is dictated by Griffith's theory of crack propagation. To mitigate product failure, adequate dispersion is imperative. We have recently quantified the extent of dispersion through USAXS measurements by using a colloidal analogy to these non-equilibrium systems.[1,2,3] Filler dispersion is dictated by the total accumulated strain as an analogy to thermal motion and temperature. Additionally, these composites display a complex hierarchical structure intimately tied to their inherent incompatibility and the processing history.[4] On the nano-scale carbon black displays primary particles aggregated into mass fractal aggregates. These aggregates are dispersed in processing and at concentrations above about 5 vol.% in the amorphous regions (or 1.5% for the total sample) local percolation of these aggregates is observed within clusters. Percolation is confined to the nano-scale since these aggregates are incompatible with the matrix PE melt leading to formation of meso-scale clusters at about 20 vol % in the amorphous phase (for a 70% crystallinity sample this corresponds to 6 vol % for the sample).

We wish to study the impact of polyethylene crystallization on the carbon distribution and dispersion which is the basis for thermally responsive high voltage fuses (Raychem). Below the melting temperature, the carbon black percolates within the amorphous regions forming a conductive pathway. In the melt, the carbon black particles un-percolate serving, breaking the conductivity pathway and acting as a surge suppressor. For high voltage systems polymer melting occurs due to resistive heating. We wish to determine the impact of this nano-scale structural rearrangement on the rheological behavior for improved melt compounding, modulus and fracture toughness for superior product performance. The structural emergence will be studied with ultra-small angle X-ray scattering and cryo TEM as well as using dielectric spectroscopy measurements to observe bulk percolation of the carbon particles. The aim is to control the multi-hierarchical structure and to correlate this with fracture toughness and UV absorption.

The proposed study serves to address several issues. First is just quantifying dispersion of carbon black in these materials through concentration gradients in the semi-crystalline and melt states. The industrial approach to determine the quality of dispersion remains largely empirical and based mostly on macroscopic scales, while carbon black is a nano-material. We have attempted to quantify filler dispersion based on a pseudo-thermodynamic approach wherein the accumulated strain imparted during mixing is analogous to thermal motion in colloids. Miscibility of a binary system in terms of the second virial coefficient is generally considered in colloidal mixtures.[1-3] The virial expansion is used to describe deviations from ideal osmotic pressure conditions using a power series expansion.[4] Dilute USAXS curves from

previous studies were fit using the Unified Scattering Function.[5-6] It has been shown that a percolation threshold is reached under semi-dilute filler conditions. Above this threshold the concentration normalized intensity, $I(q)/\phi$, decreases in the low-q regime due to structural screening and the large-scale structure of the aggregates cannot be seen due to overlap of the filler particles.[7-9] The rate at which $I(q)/\phi$ decreases with concentration at low-q is a measure of the second virial coefficient.

For polymer matrices such as HDPE, that display correlation peaks due to crystalline lamellae, no accurate fitting model exists in literature. This presents a formidable challenge towards quantifying dispersion. We wish to mitigate this by considering the packing, long period, orientation and disorder in stacked crystal lamellae in our fitting model. These parameters can then be used to determine the pseudo-second virial coefficient (A_2) under semi-dilute conditions subject to control by shear rate, screw geometry and carbon black grades. A_2 can be translated to repulsive interaction potentials for coarse-grained modeling of these systems.

Second is the impact of polyethylene crystallization on the carbon black distribution. Although the carbon black percolation below melting temperature and subsequent disruption of the conductive pathways is known, controlling the structural emergence by altering polymer crystallinity and its impact on compounding, modulus and fracture toughness is not well known.

A carbon black masterbatch (HPDE matrix) will be extruded with a suitable polyethylene base resin while varying the processing conditions such as screw speed and screw geometry to vary the overall accumulated strain. Additionally, we plan on using masterbatches with two different grades of carbon black. The samples will be mounted on a heating block that will be maintained above the melting temperature and then annealed while recording USAXS / SAXS measurements.

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