Nano-Maufacturing

One View of NM

Quantification of nano-dispersion in polymer nanocomposites: A thermodynamic analogy

Greg Beaucage
Professor of Chemical and Materials Engineering

Kabir Rishi
CDC/NIOSH Research Laboratory, Cincinnati Ohio

Department of Materials Science & Engineering
University of Cincinnati

Nano-Maufacturing

One View of NM

A Desired Property: Dynamic Mechanical Spectrum

A Nano Solution: Precipitated Silica

Nano->Colloidal->Micro->Macroscopic

Proposition: Nano-Manufacturing Involves Hierarchy

The Challenge is to Build Hierarchy

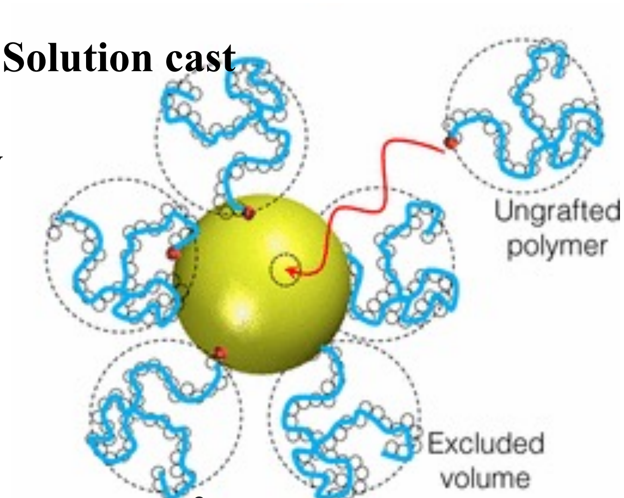
Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

Current academic state-of-the-art nanocomposite

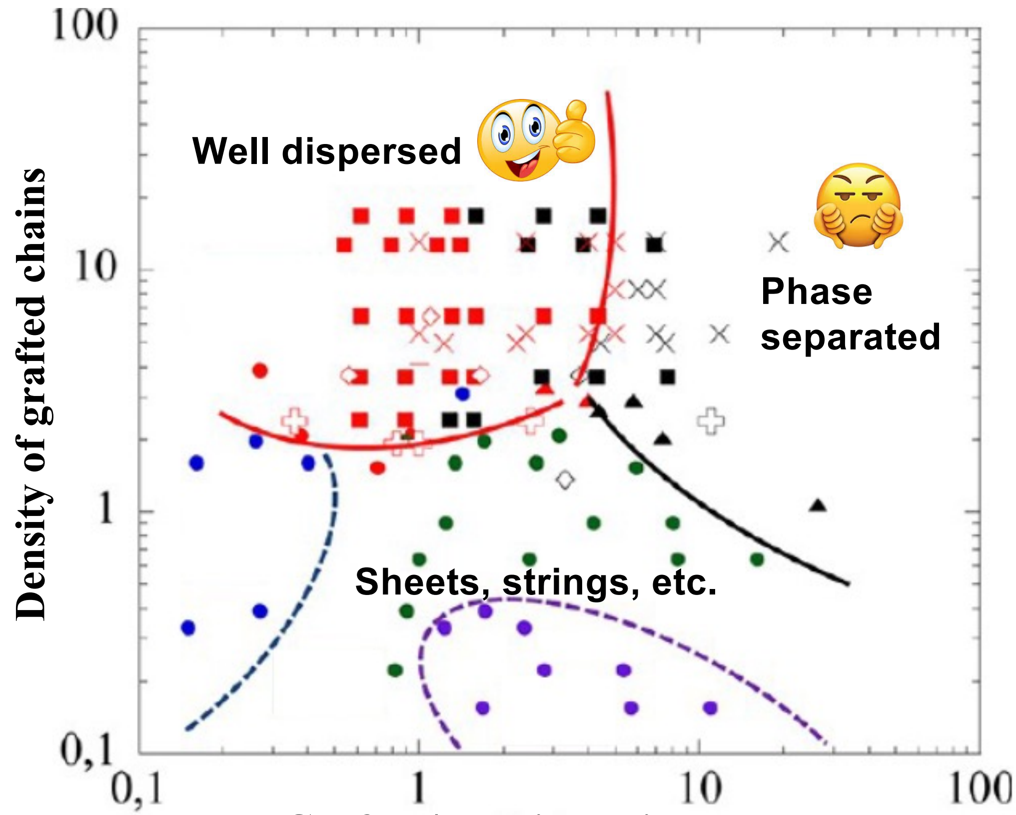
Monodisperse colloidal particles

Colloidal Solution cast

Thermally Dispersed



50Å



Objective:

Enhance miscibility (i.e. no hierarchy)

Kumar, S.K., Jouault, N., Benicewicz, B. and Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules*, *46*(9), pp.3199-3214.

Kumar, S.K., Benicewicz, B.C., Vaia, R.A. and Winey, K.I., 2017. 50th anniversary perspective: are polymer nanocomposites practical for applications?. *Macromolecules*, *50*(3), pp.714-731.

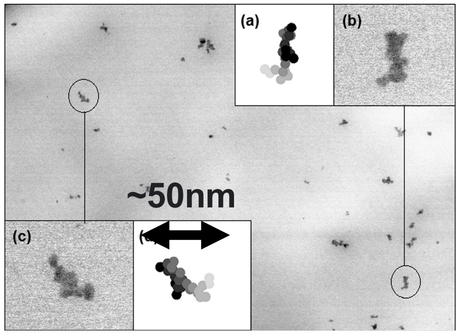
Asai, M., Zhao, D. and Kumar, S.K., 2017. Role of grafting mechanism on the polymer coverage and self-assembly of hairy nanoparticles. *ACS Nano*, *11*(7), pp.7028-7035.

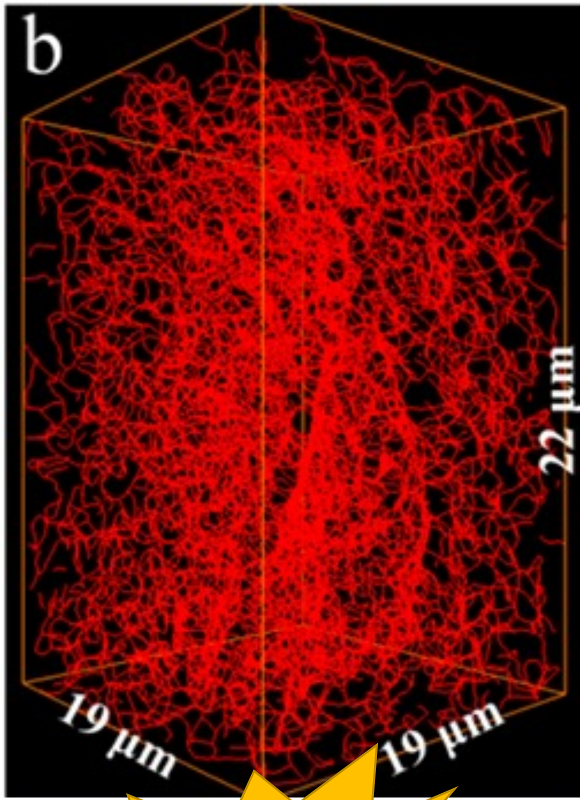
The original nanocomposite

Polydisperse aggregates

Processed under shear

Kinetically mixed **immiscible**





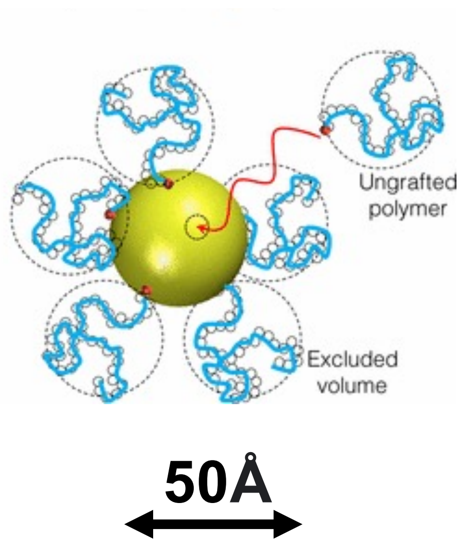
Objective:
Tear resistance
Static charge dissipation
Dynamic mechanical spectrum

Why/how do added nanoparticles impact structures 100-1,000 times larger?

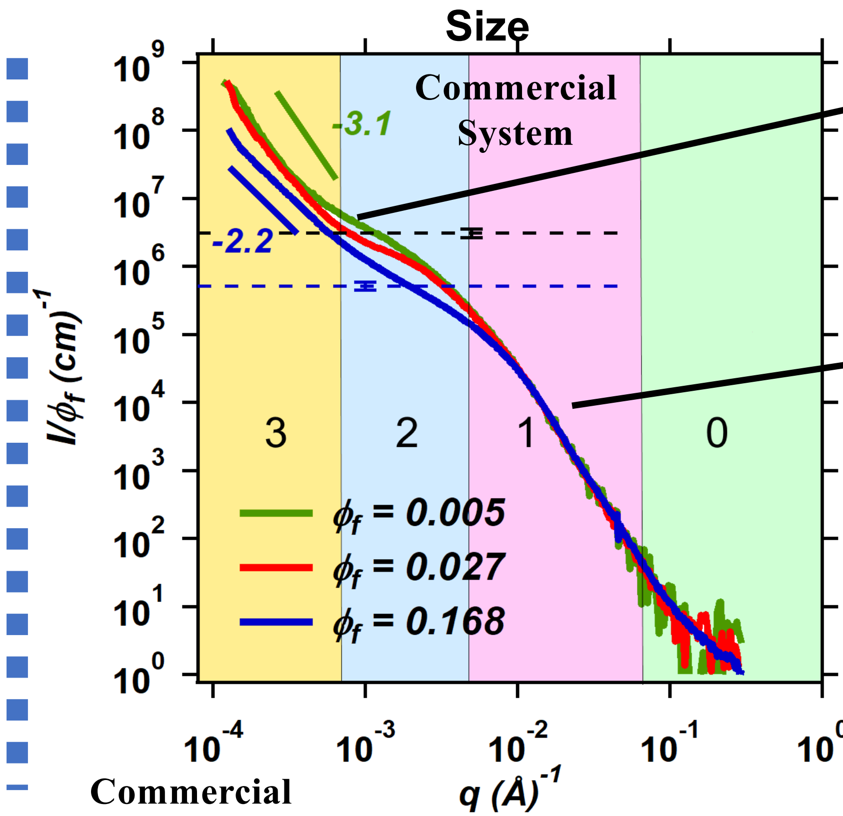
1,000 x larger

Song, L; Wang, Z; Tang, X.; Chen, L.; Chen, P.; Yuan, Q.; **Li, L.** Visualizing the Toughening Mechanism of Nanofiller with 3D X-ray Nano-CT: Stress-Induced Phase Separation of Silica Nanofiller and Silicone Polymer Double Networks Macromolecules 50 7249-7257 (2017).

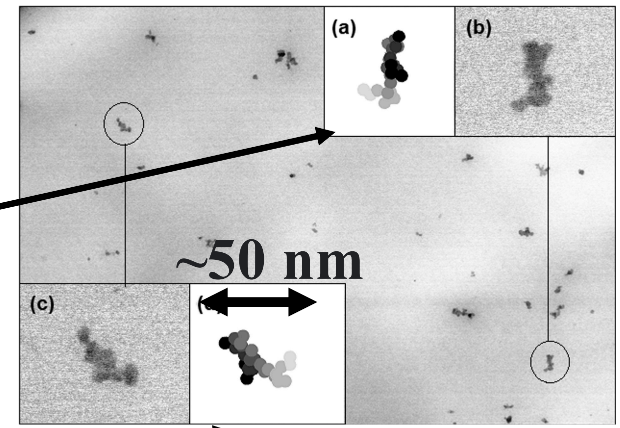
Multiscale Hierarchical Structures



State of the Art
Model System



Commercial
System

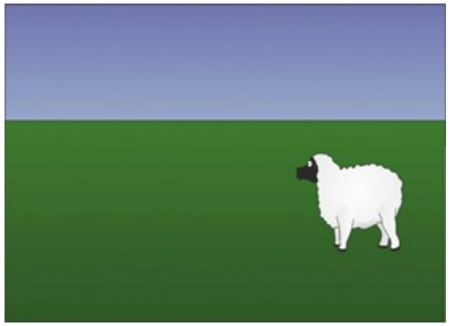


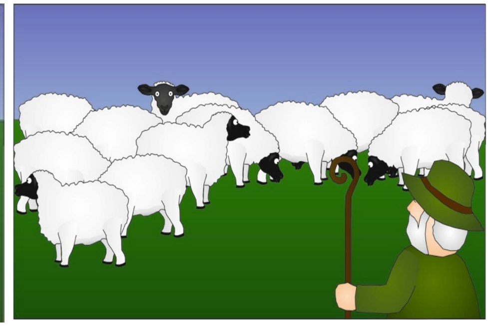
Aggregates of primary particles

One size scale vs. multiple hierarchical size scales

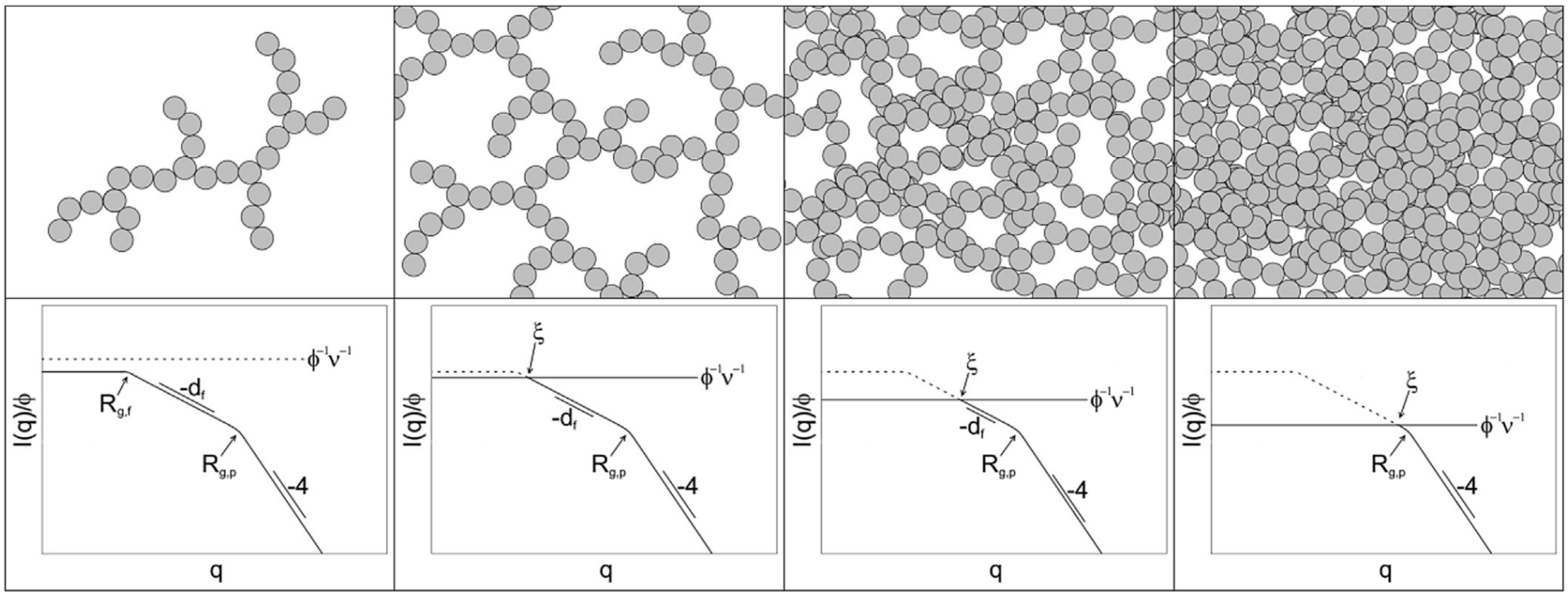
Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.
Mulderig, A., Beaucage, G., Vogtt, K., Jiang, H. and Kuppa, V., 2017. Quantification of branching in fumed silica. *Journal of Aerosol Science*, *109*, pp.28-37.

A_2 (or B_2) from scattering





Quantitative measure of nano-dispersion

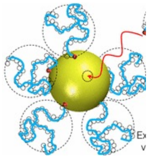


Pedersen, J. S.; Sommer, C. Temperature Dependence of the Virial Coefficients and the Chi Parameter in Semi-Dilute Solutions of PEG. In *Scattering Methods and the Properties of Polymer Materials*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2005; pp 70–78.

Vogtt, K.; Beaucage, G.; Weaver, M.; Jiang, H. Thermodynamic Stability of Worm-like Micelle Solutions. *Soft Matter* 2017, *13* (36), 6068–6078.

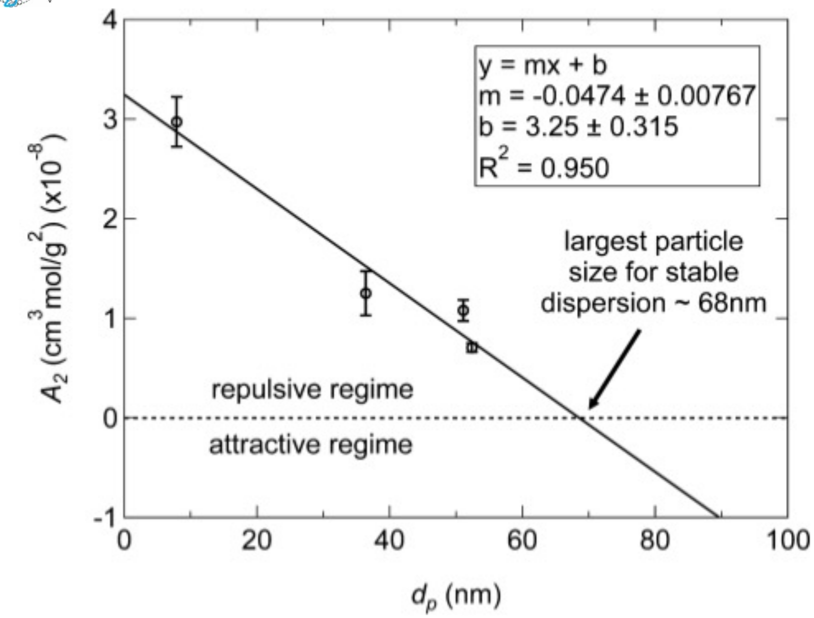
Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; Narayanan, V. A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer (Guildf).* 2017, *129*, 32–43.

Thermal Dispersion versus Kinetic Dispersion



Miscible:

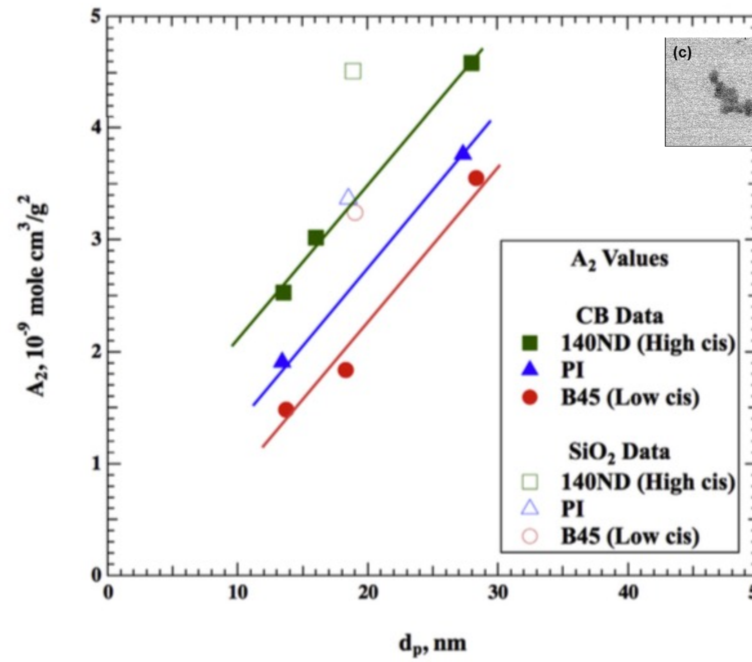
Organic Pigment with Triton X100

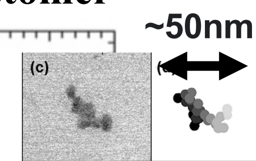


Thermally driven nano-dispersion (Stokes drag coefficient)

Immiscible:

Carbon Black and Silica in Elastomer





Mechanically driven nano-dispersion (Lever arm)

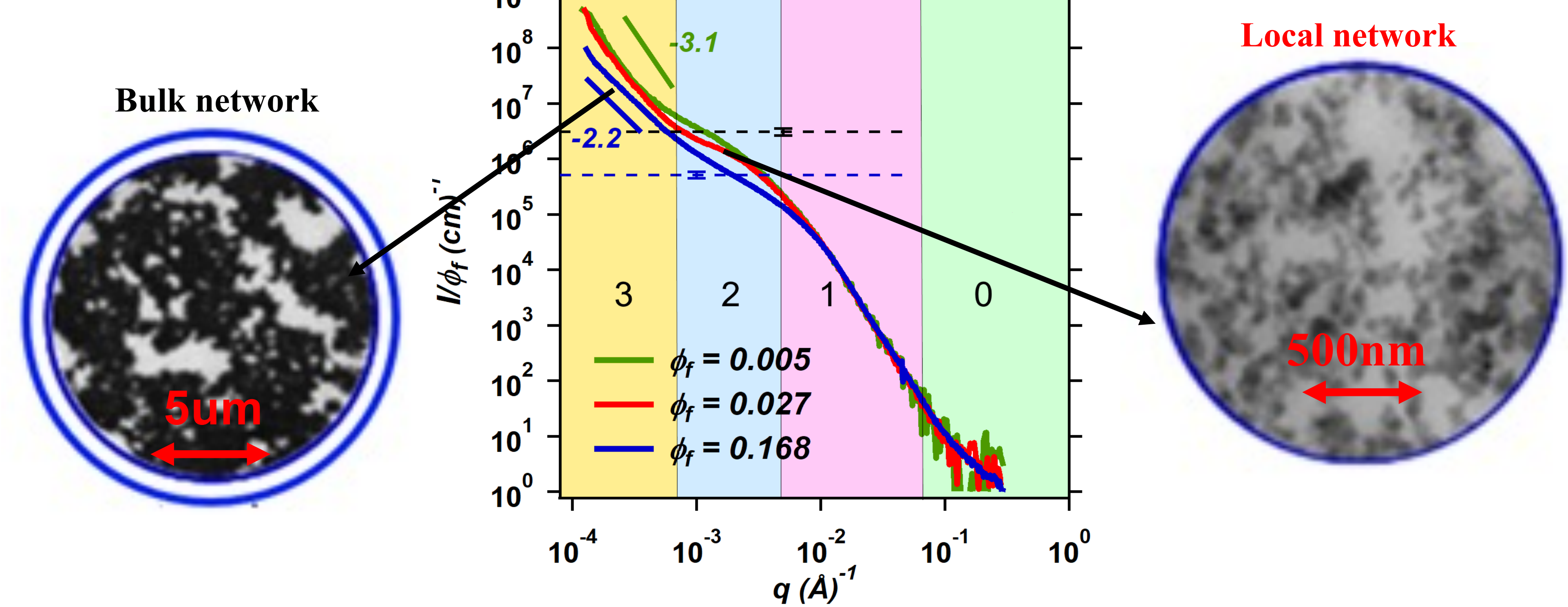
Mulderig, A.; Beaucage, G.; Vogtt, K.; Jiang, H.; Jin, Y.; Clapp, L.; Henderson, D. C. Structural Emergence in Particle Dispersions. *Langmuir* **2017**, *33* (49), 14029–14037.
Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; Narayanan, V. A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer (Guildf).* **2017**, *129*, 32–43.

Clustering can lead to locally higher concentrations

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

Multiscale Hierarchical Structures

Immiscibility forms clusters

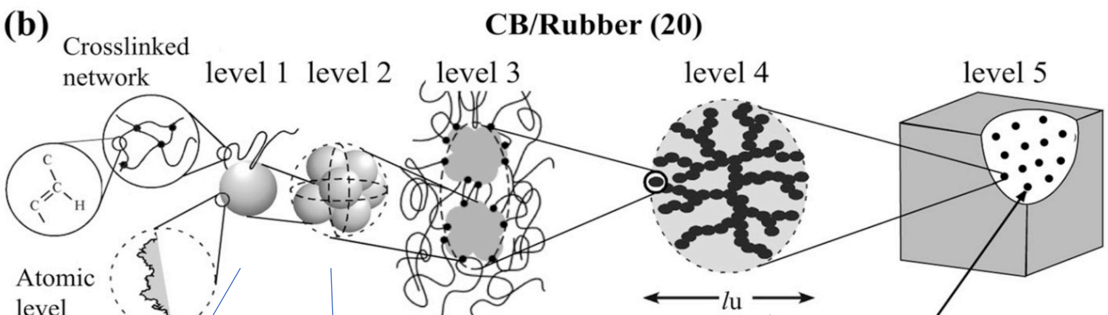


Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

Trappe, V. and Weitz, D.A., 2000. Scaling of the viscoelasticity of weakly attractive particles. *Physical review letters*, *85*(2), p.449.

Mulderig, A., Beaucage, G., Vogtt, K., Jiang, H. and Kuppa, V., 2017. Quantification of branching in fumed silica. *Journal of Aerosol Science*, *109*, pp.28-37.

Multiscale Hierarchical Structures

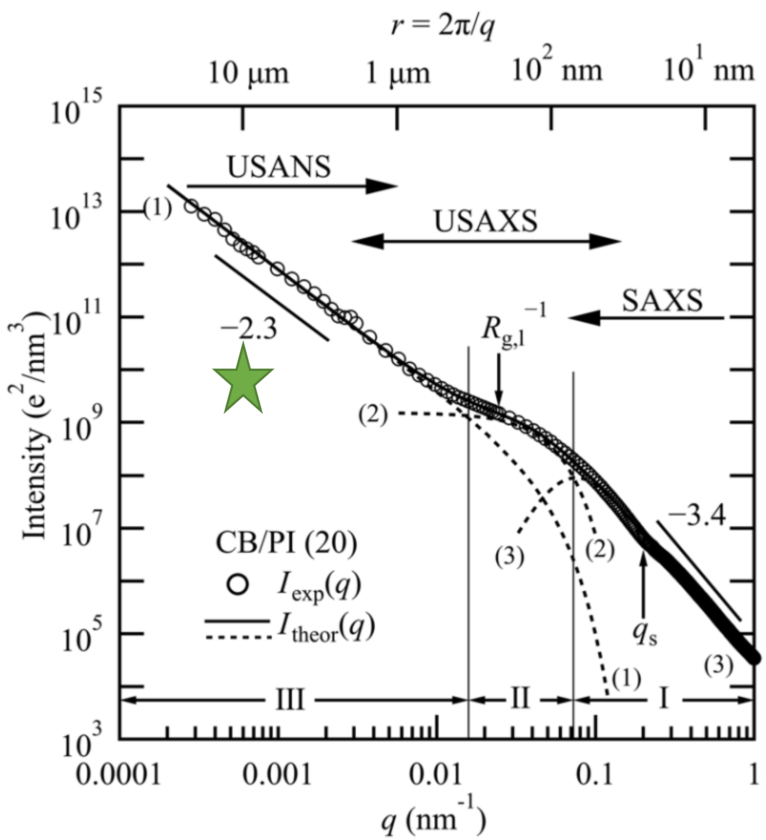


Primary Particles

Aggregates

Local network

Bulk network



Hashimoto, T., Amino, N., Nishitsuji, S. and Takenaka, M., **2019**. Hierarchically self-organized filler particles in polymers: cascade evolution of dissipative structures to ordered structures. *Polymer Journal*, *51*(2), pp.109-130.

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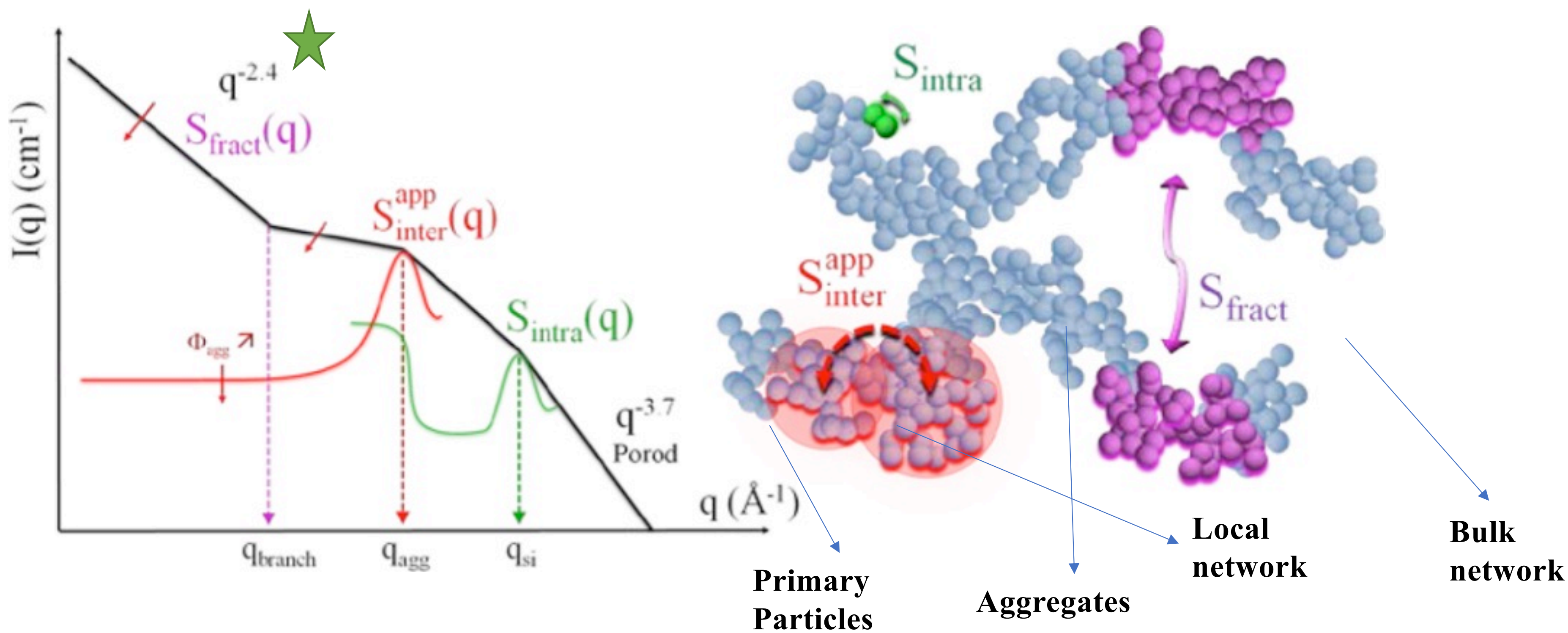
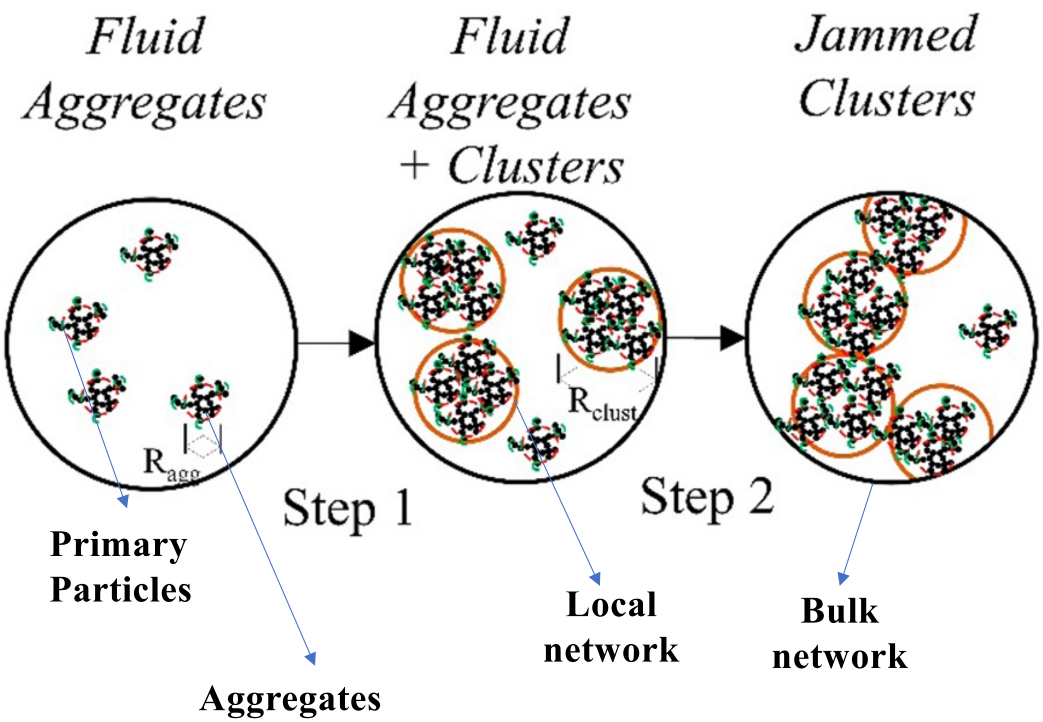
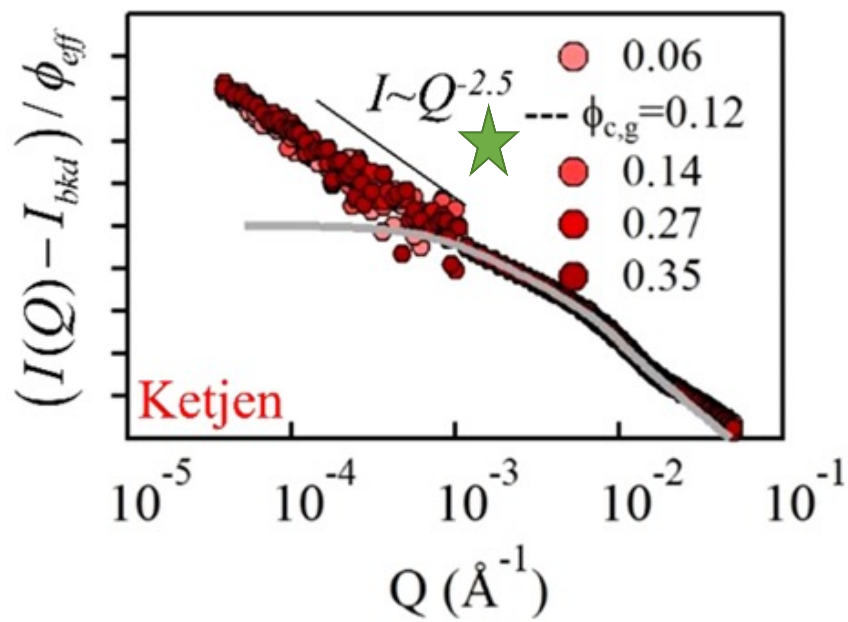
Multiscale Hierarchical Structures



Baeza, G.P., Genix, A.C., Degrandcourt, C., Petitjean, L., Gummel, J., Couty, M. and Oberdisse, J. *Multiscale filler structure in simplified industrial nanocomposite silica/SBR systems studied by SAXS and TEM.* Macromolecules ***46*** 317-329 (2013).

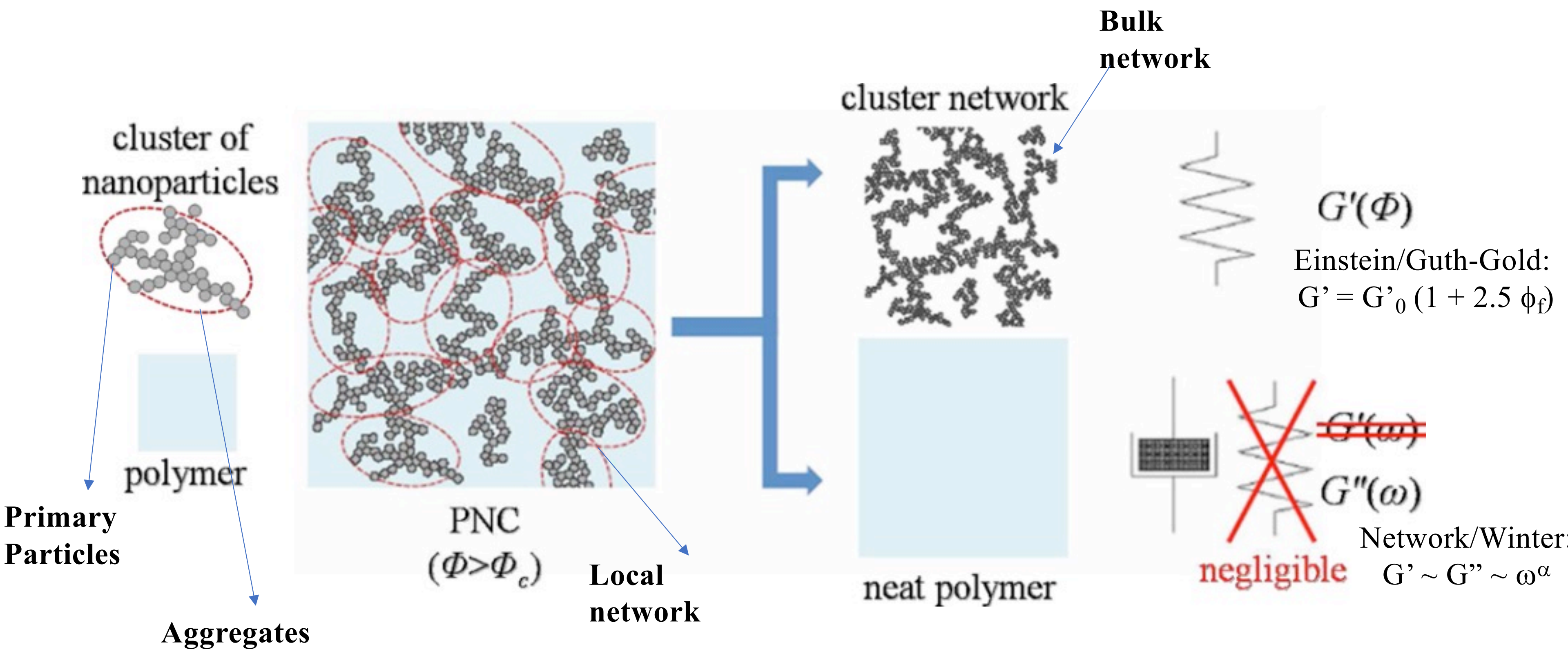
Multiscale Hierarchical Structures





Richards, J.J., Hipp, J.B., Riley, J.K., Wagner, N.J. and Butler, P.D. *Clustering and percolation in suspensions of carbon black.* Langmuir **33** 12260-12266 (2017).

Multiscale Hierarchical Structures



Filippone, G., Romeo, G. and Acierno, D. *Viscoelasticity and structure of polystyrene/fumed silica nanocomposites: filler network and hydrodynamic contributions.* Langmuir **26** 2714-2720 (2010).
Filippone, G. and Salzano de Luna, M. *A unifying approach for the linear viscoelasticity of polymer nanocomposites.* Macromolecules **45** 8853-8860 (2012).

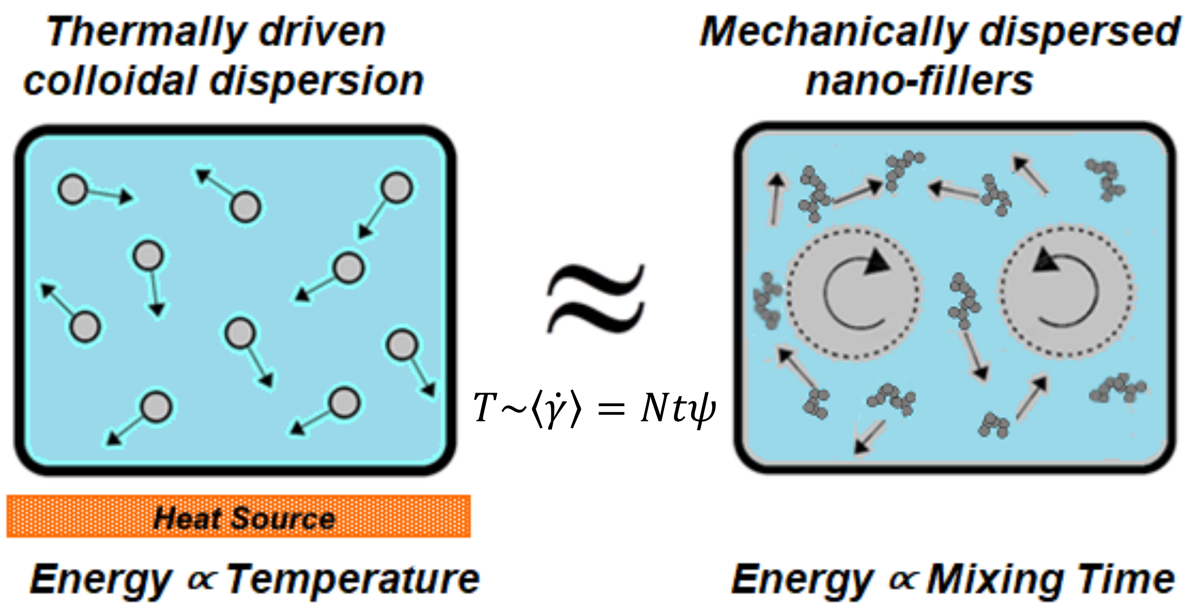
Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

van der Waals model for incompatible polymer nanocomposites

a reflects the attractive energy of interaction between aggregates.

$$\Pi = \frac{RT}{(V+b)} - \frac{a}{V^2}$$

b is the excluded volume



$$T \sim \langle \dot{\gamma} \rangle = Nt\psi$$

$$A_2(T) = \frac{N_A}{M^2}\left(b - \frac{a}{kT}\right)$$

$$A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)$$

Rishi, K.; Narayanan, V.; Beaucage, G.; McGlasson, A.; Kuppa, V.; Ilavsky, J.; Rackaitis, M. *A Thermal Model to Describe Kinetic Dispersion in Rubber Nanocomposites: The Effect of Mixing Time on Dispersion.* Polymer **175** 272–282 (2019).

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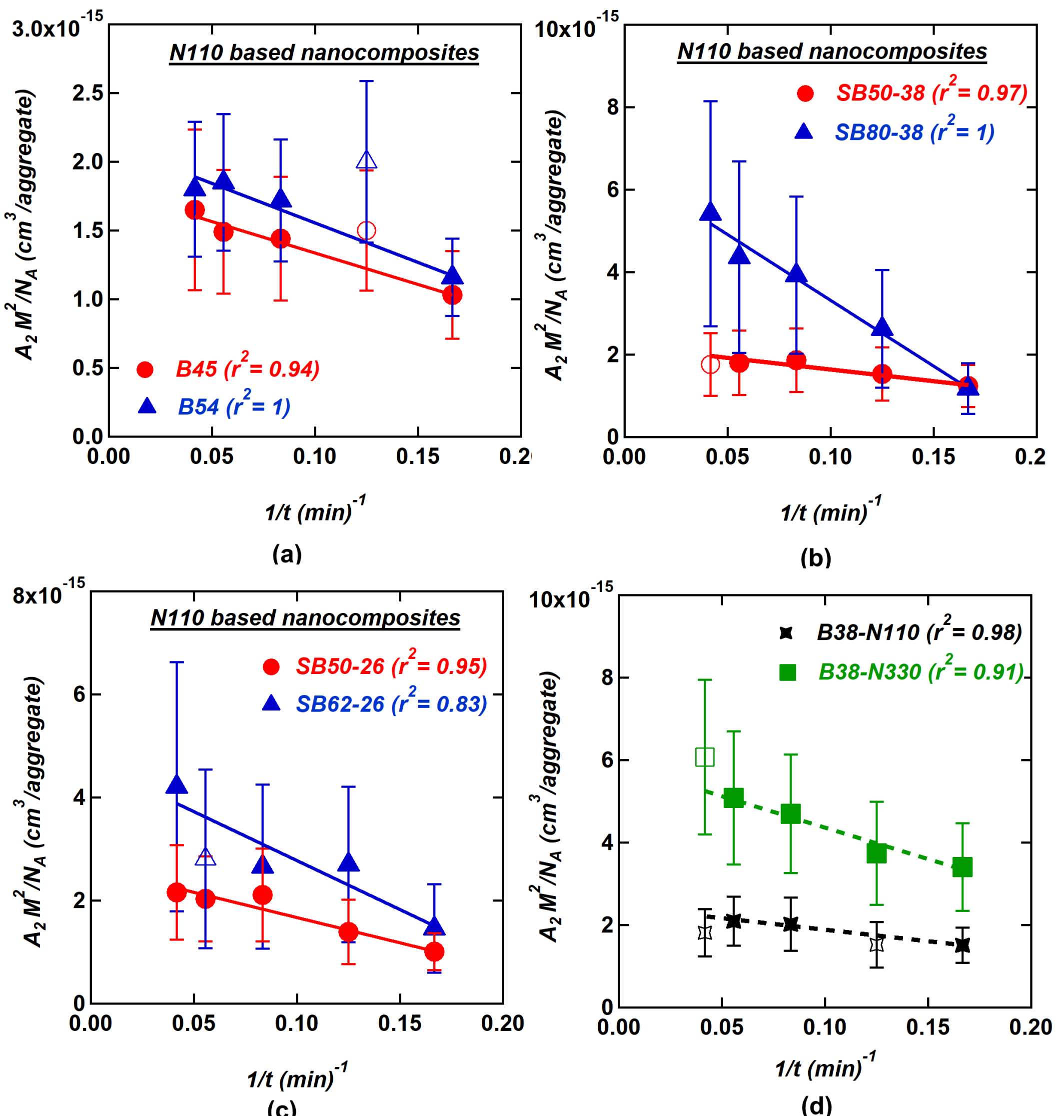

Van der Waals approach seems viable

$$A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)$$

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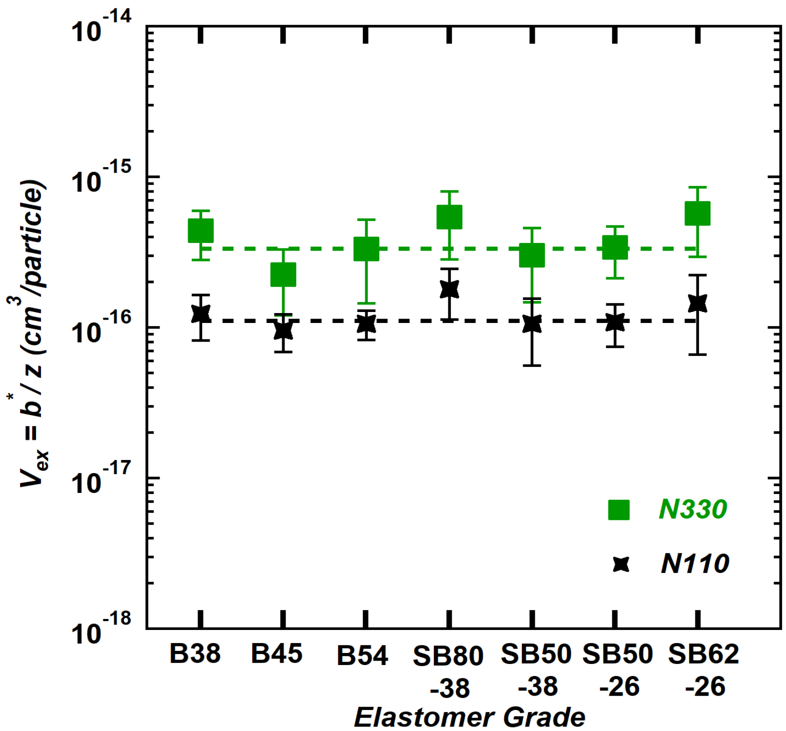
Excluded volume is associated with the occupied volume of an aggregate.
$(d_{p,N330}/d_{p,N110})^3 = 4.2$



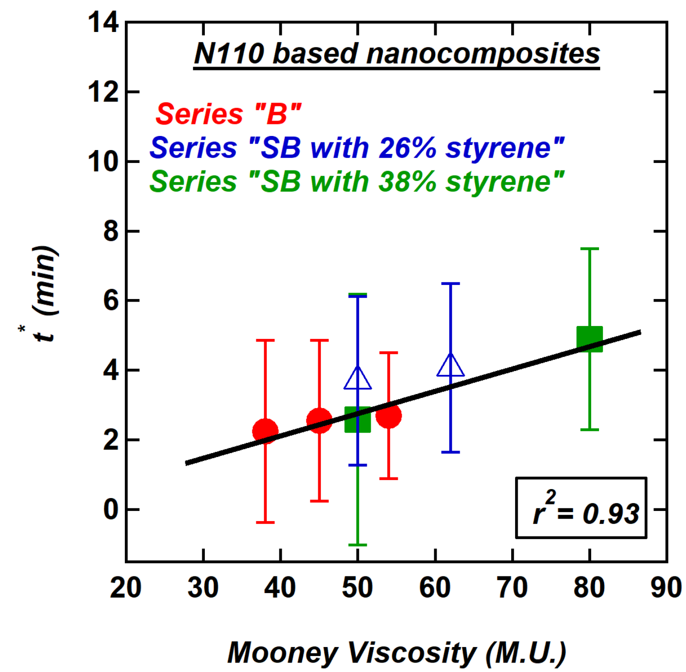
N110	Vulcan 8 (Cabot)	123 m²/g	25.7 nm
N330	Vulcan 3 (Cabot)	76 m²/g	41.6 nm

$$A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)$$

Wetting time depends on **viscosity** and **primary particle size**

x-intercept reflects "wetting time"

$$A_2 = 0, \quad t^* = a^*/b^*$$



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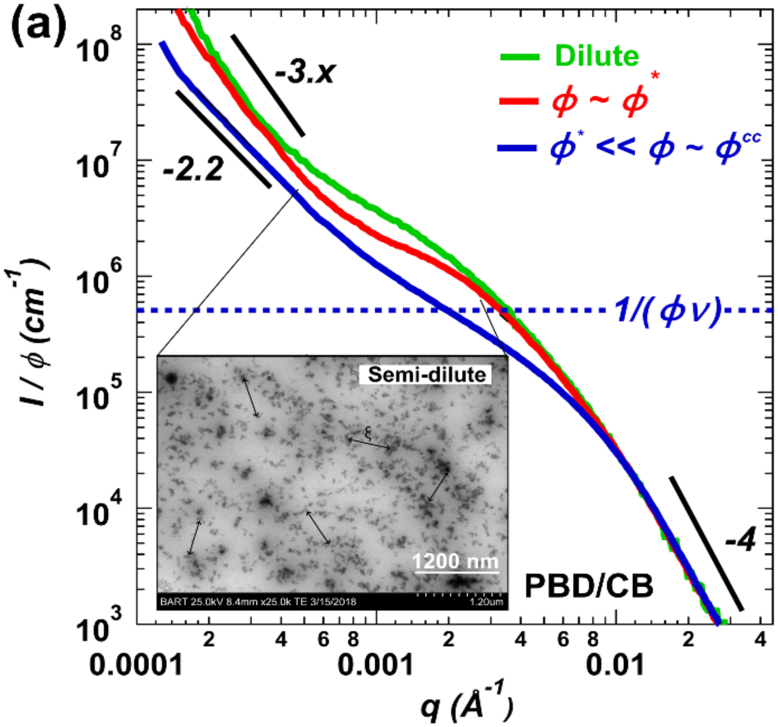
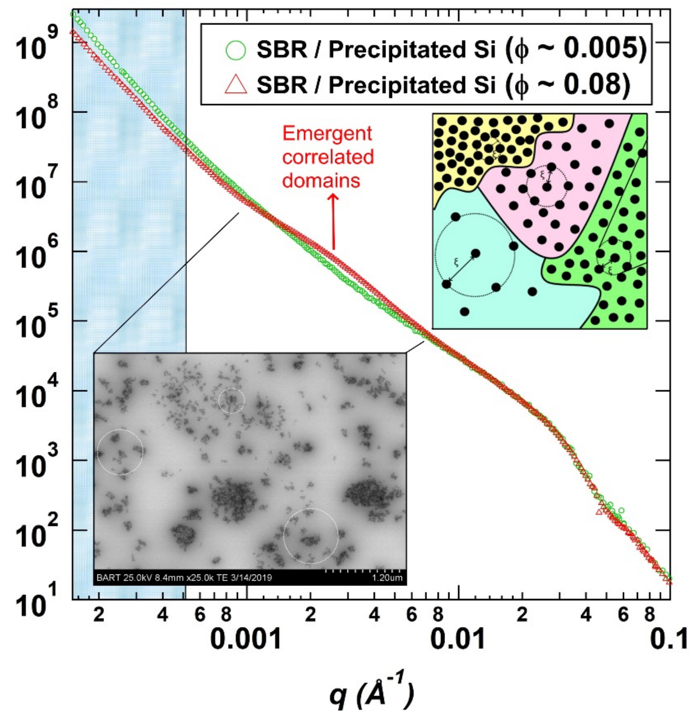
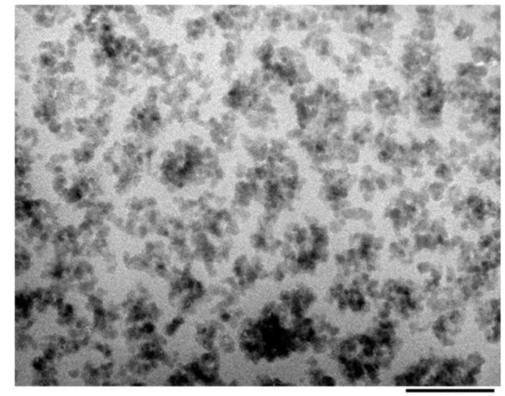
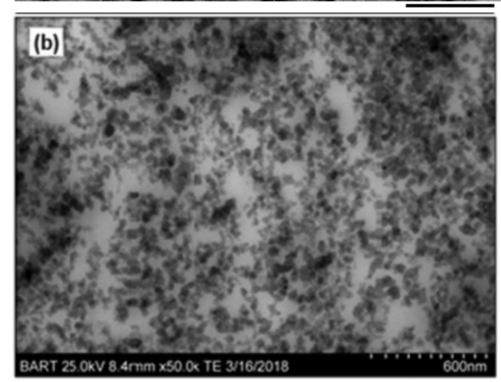
Mean field (CB) and specific interactions (Silica)









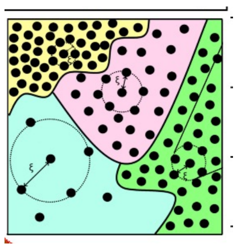
McGlasson, A., Rishi, K., Beaucage, G., Chauby, M., Kuppa, V., Ilavsky, J. and Rackaitis, M., 2020. Quantification of dispersion for weakly and strongly correlated nanofillers in polymer nanocomposites. *Macromolecules*, *53*(6), pp.2235-2248.

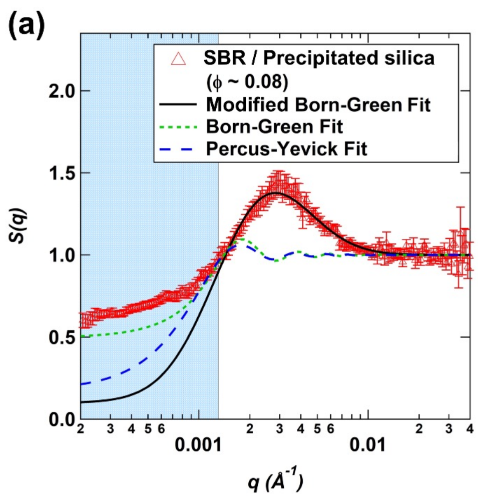
Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

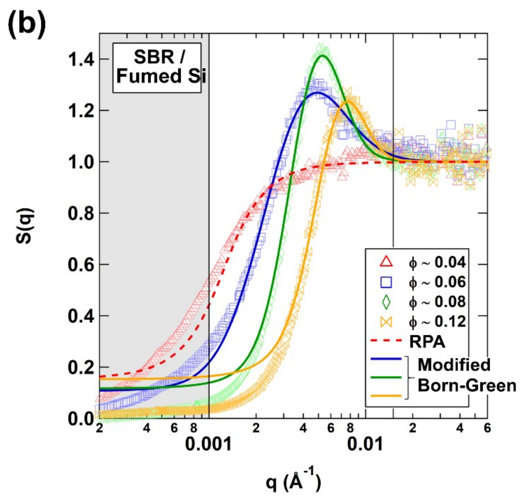
Specific interactions (Silica)

Positive a^* can lead to correlated silica aggregates, New scattering function to fit these curves (solves an impossible task)





Adapted from McGlasson, A., Rishi, K., Beaucage, G., Chauby, M., Kuppa, V., Ilavsky, J. & Rackaitis, M. Quantification of Dispersion for Weakly and Strongly Correlated Nanofillers in Polymer Nanocomposites. Macromolecules 53, 2235–2248 (2020).



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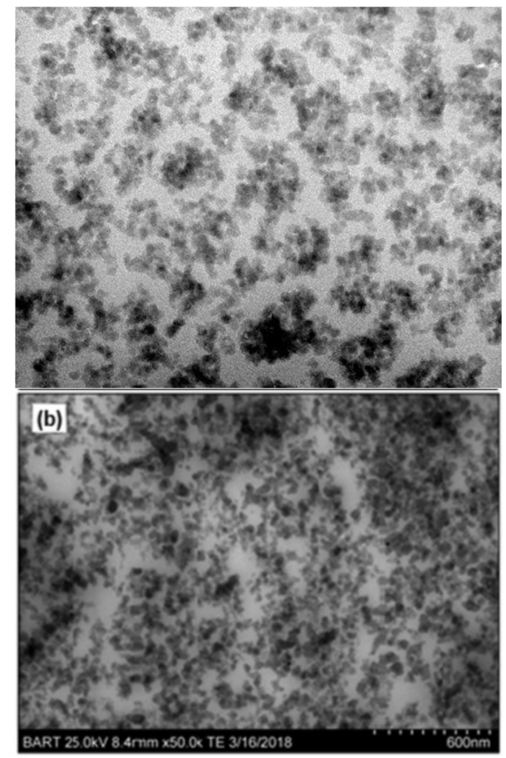

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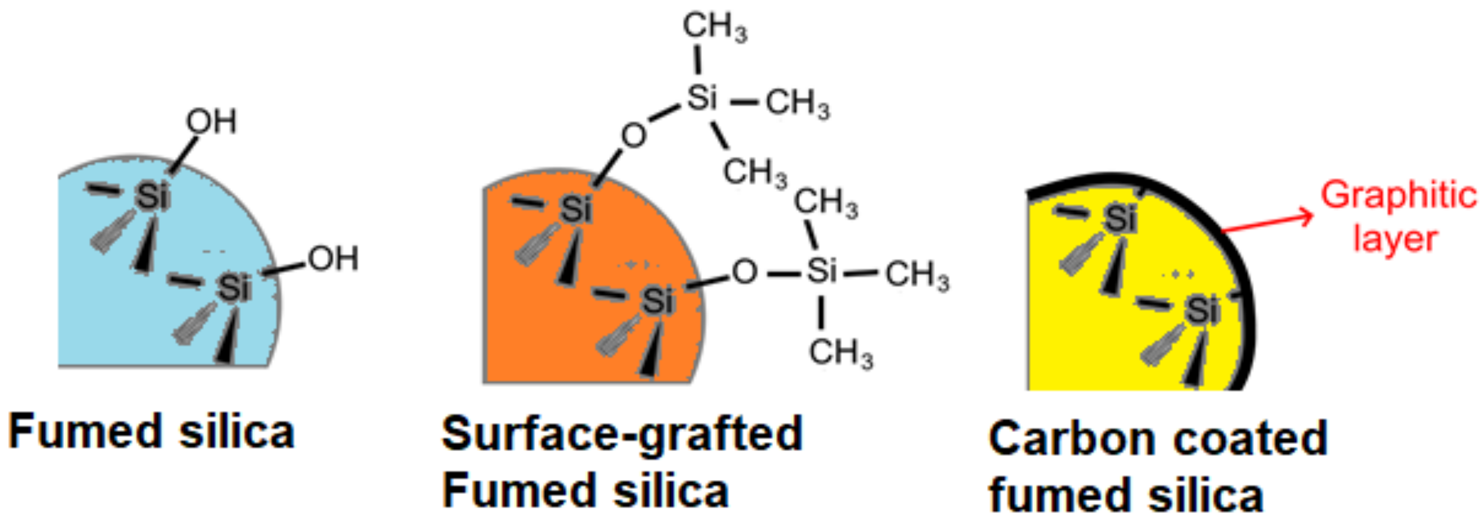
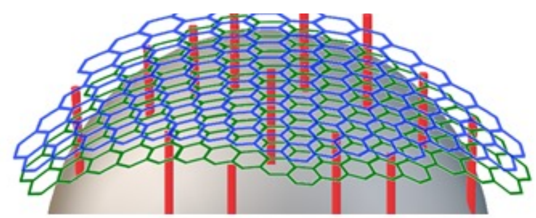
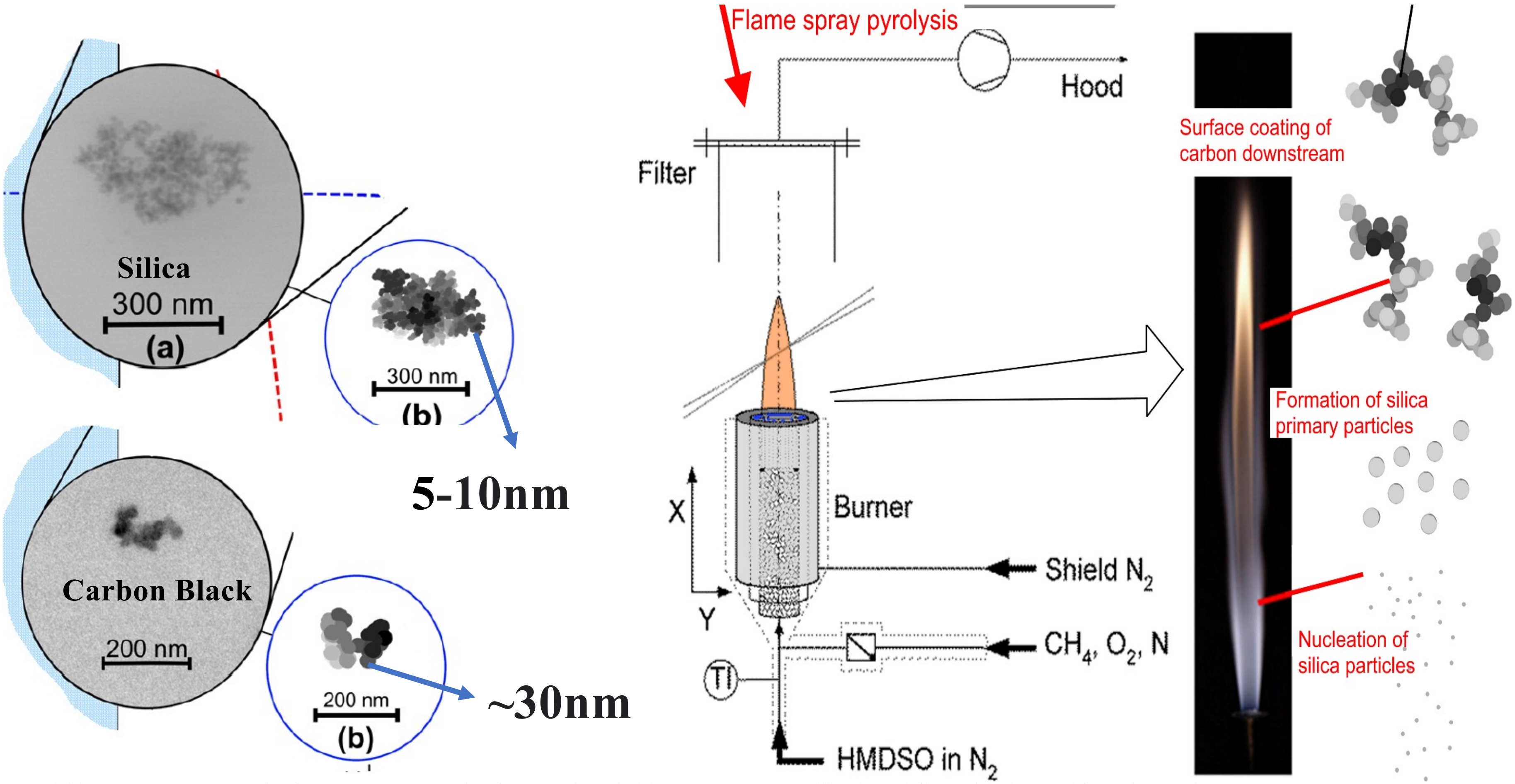
Aggregates to Clusters

Control <u>immiscibility</u> through surface modification





Okoli, U.; Rishi, K.; Beaucage, G.; Kammler, H. K.; McGlasson, A.; Michael, C.; Narayanan, V.; Grammens, J. *Dispersion and Dynamic Response for Flame-Synthesized and Chemically Modified Pyrogenic Silica in Rubber Nanocomposites*; 2022. Submitted to *Composites Sci. & Tech.*.



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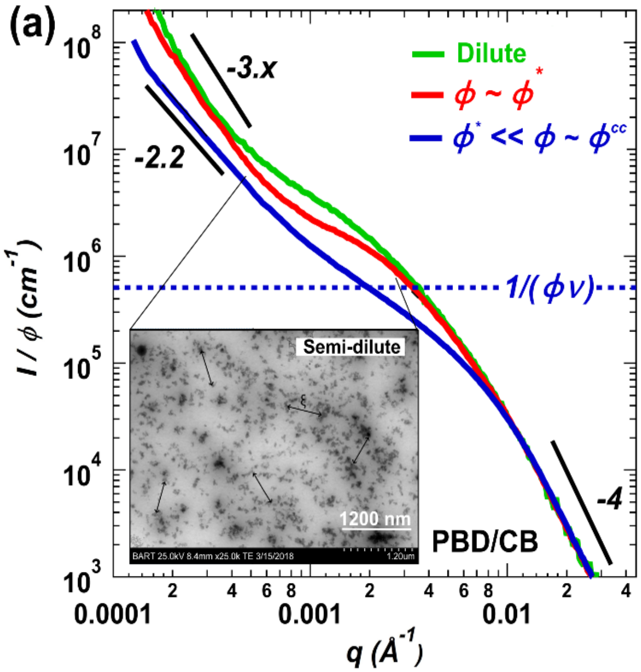
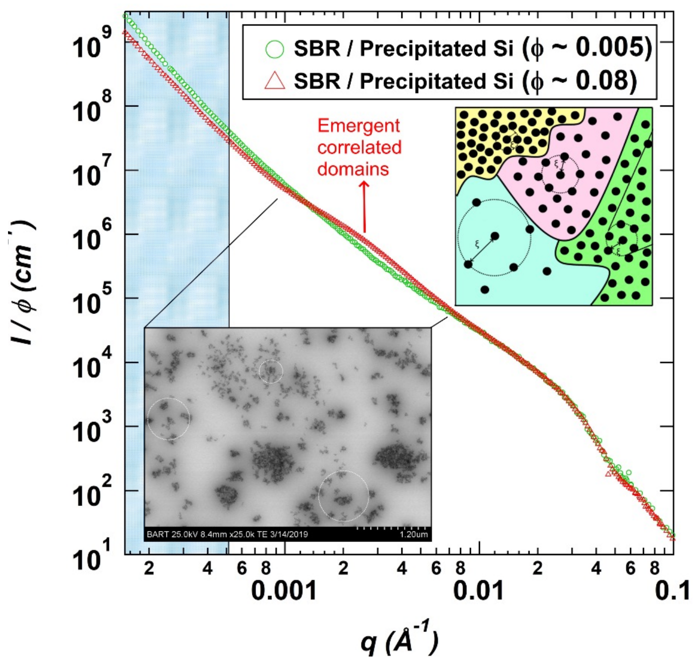
Clustered aggregates to bulk network

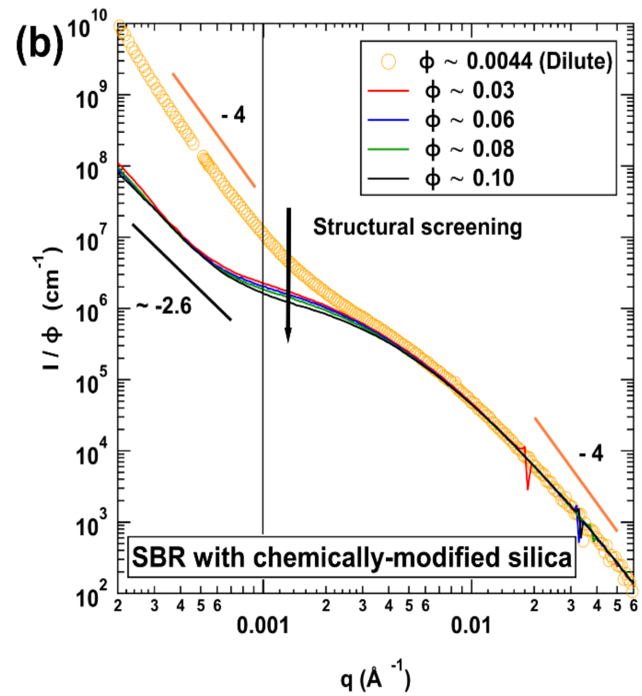
Carbon Black/Mean Field



Silica/Specific Interactions



Carbon Coated Silica/Mean Field



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Surface Modification for Controlled Immiscibility

$$A_2(t) = \frac{N_A}{M^2}\left(b^* - \frac{a^*}{t}\right)$$

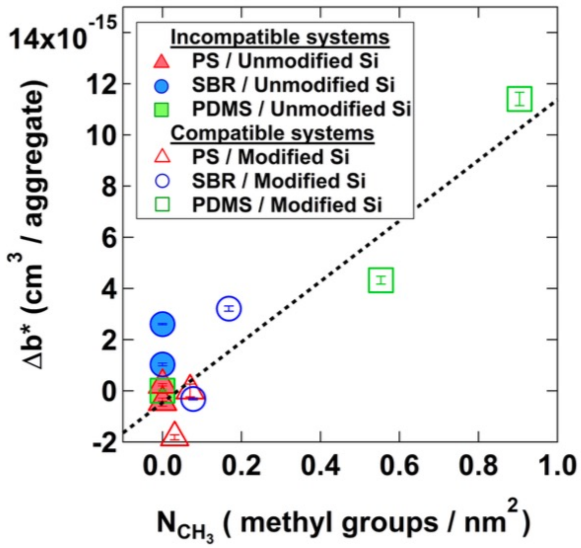


FIG. 11. A plot showing the bound polymer content (Δb^*) determined from the excluded volumes of the filler aggregates before and after dispersion as a function of surface methyl content (N_{CH_3}). The dashed line indicates that Δb^* is proportional to N_{CH_3} determined from FTIR.

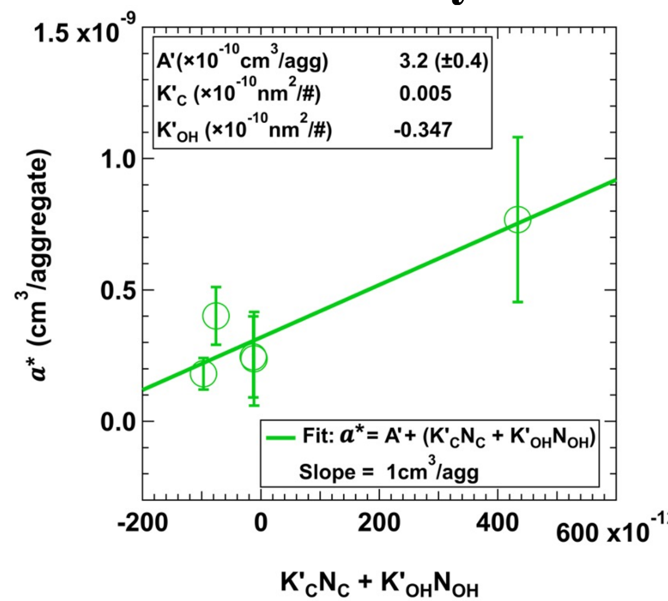
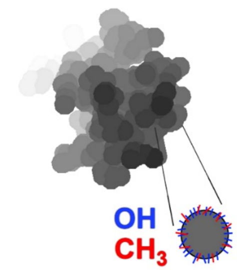


Figure 9. Plot of the particle interaction parameter, a^*, expressed in cm³/aggregate as a function of the linear sum of the surface carbon content (N_C) and surface hydroxyl content (N_{OH}) weighted differently. a^* is an attractive potential so negative values indicate relative repulsion between aggregates that increases with surface carbon content. That is, surface carbon enhances aggregate/polymer attraction relative to aggregate/aggregate attraction. The fit parameters, A', K'_C, and K'_{OH} were obtained through least squares minimization.



b^* can be calculated as the excluded volume for an aggregate, $zV_{0,}$ without bound rubber

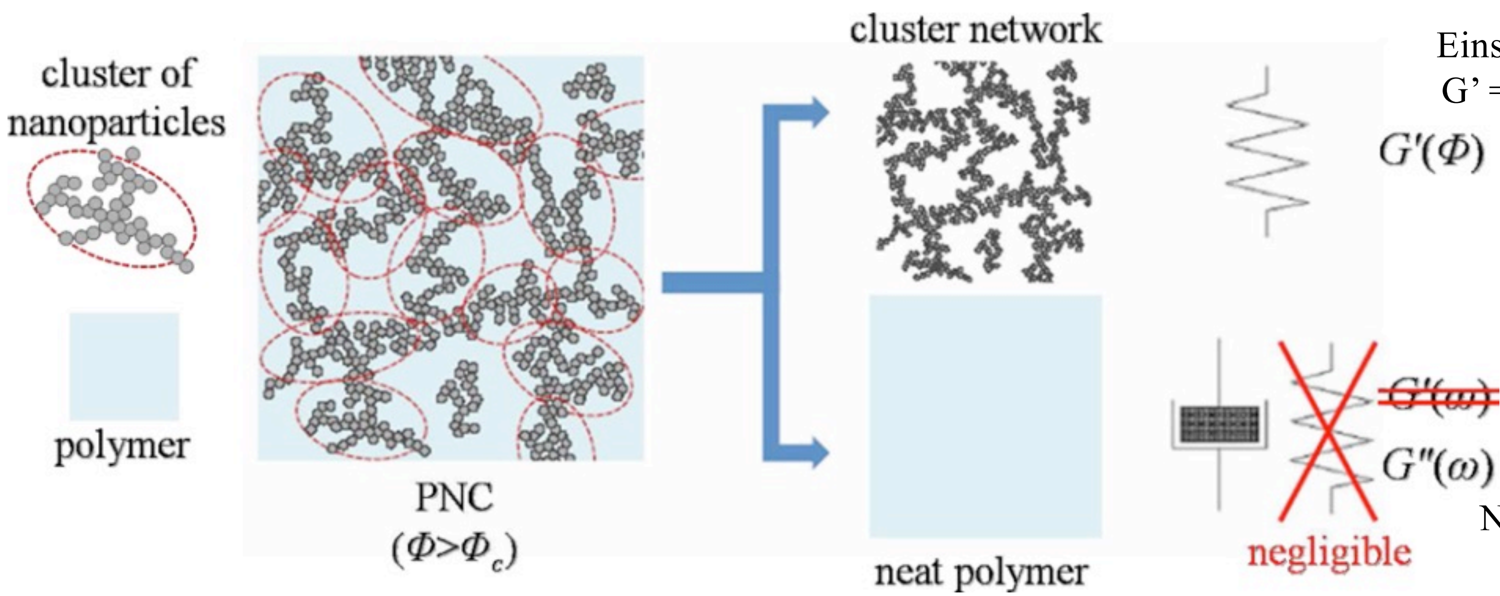
b^* increases with bound rubber.

a^* reflects the attractive energy of interaction between aggregates. $\Pi = \frac{RT}{(V+b)} - \frac{a}{V^2},$ attractive potential

Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

Morphology from rheology

- How does this multi-hierarchical model relate to oscillatory rheometry?



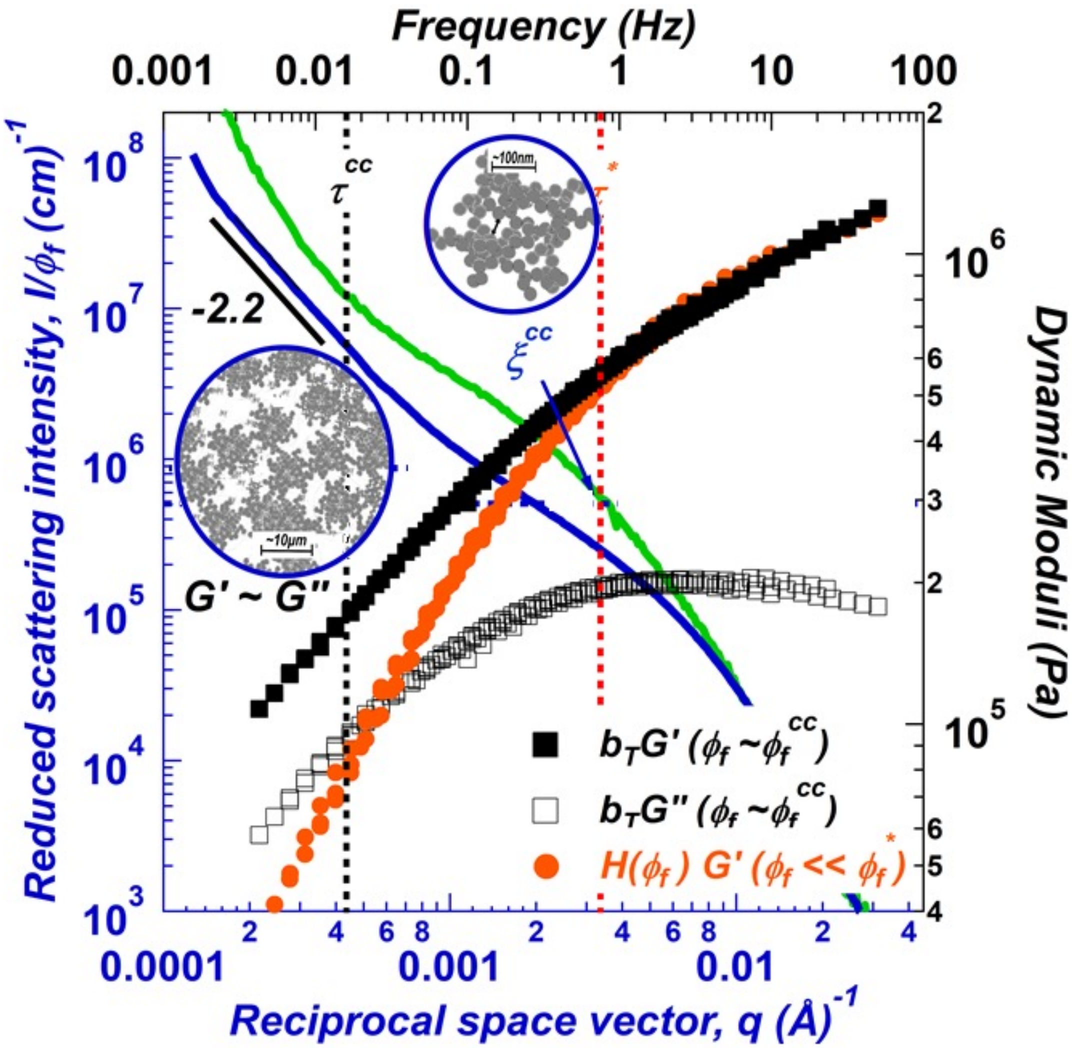
Einstein/Guth-Gold:
$G' = G'_0 (1 + 2.5\ \phi_f)$

Network/Winter:
$G' \sim G'' \sim \omega^{\alpha}$

Filippone, G., Romeo, G. and Acierno, D., 2010. Viscoelasticity and structure of polystyrene/fumed silica nanocomposites: filler network and hydrodynamic contributions. *Langmuir*, *26*(4), pp.2714-2720.

Filippone, G. and Salzano de Luna, M., 2012. A unifying approach for the linear viscoelasticity of polymer nanocomposites. *Macromolecules*, *45*(21), pp.8853-8860.

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com



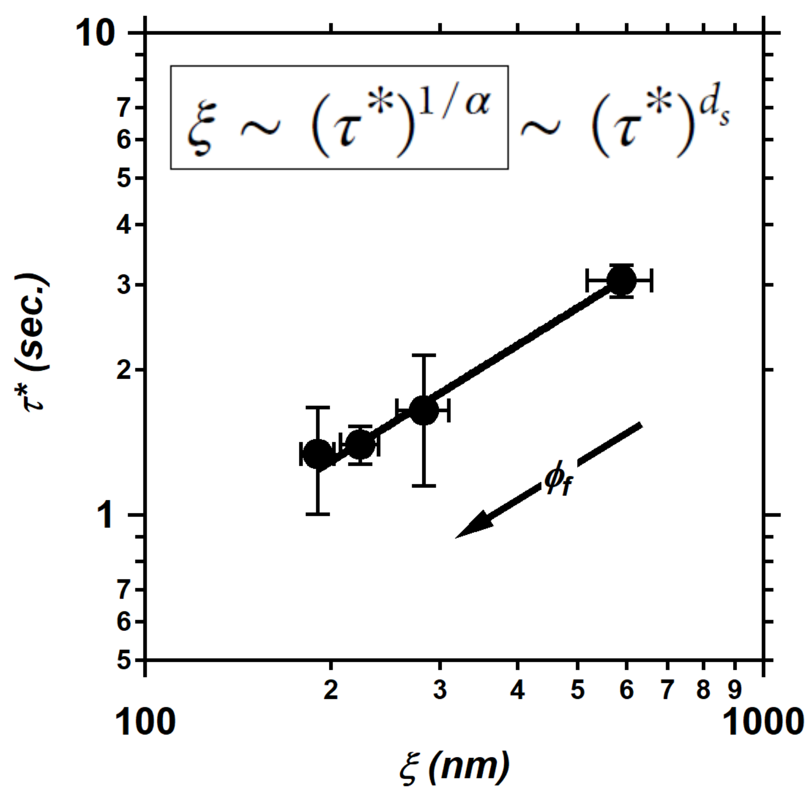
Einstein/Guth-Gold: $G' = G'_0 (1 + 2.5\ \phi_f)$

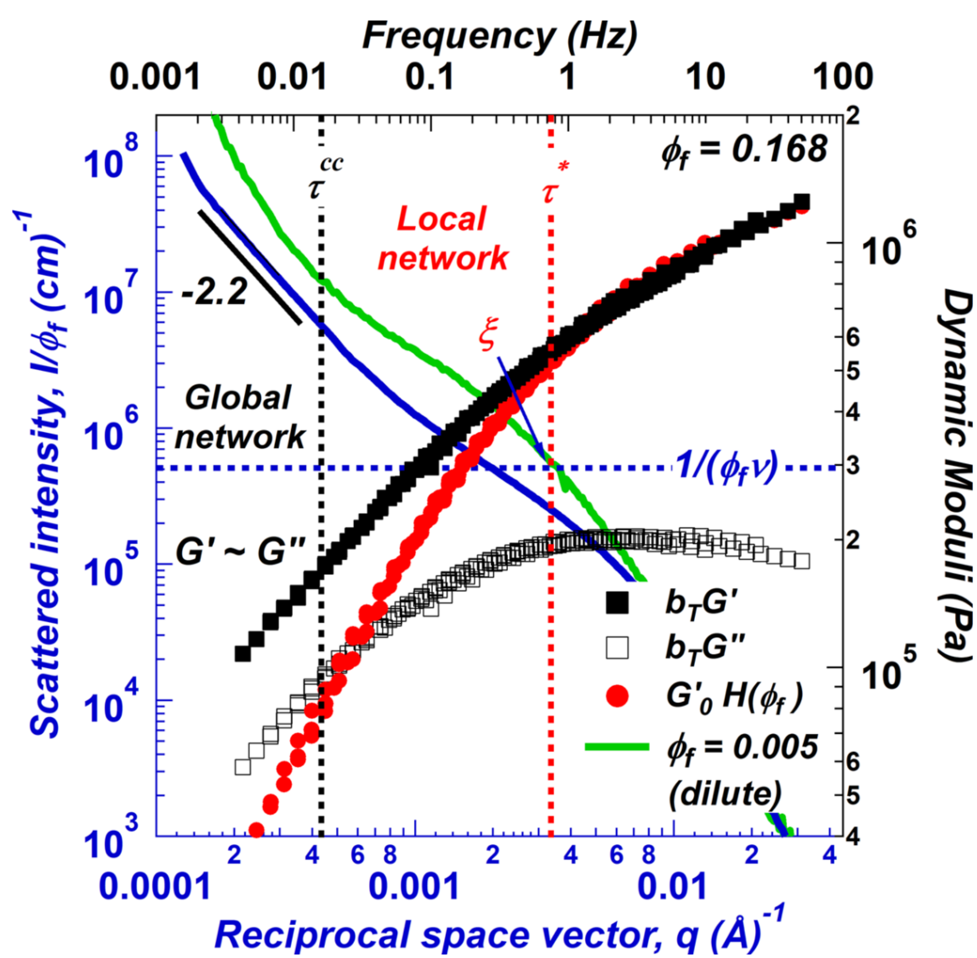
- ❖ At intermediate frequencies, deviation of semi-dilute rheology from dilute under same shear conditions ascertained by scaling dilute sample by Einstein-Smallwood factor

- ❖ At low oscillation frequencies, G'~G" indicates gel-like behavior*

Network/Winter
$G' \sim G'' \sim \omega^{\alpha}$

Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.





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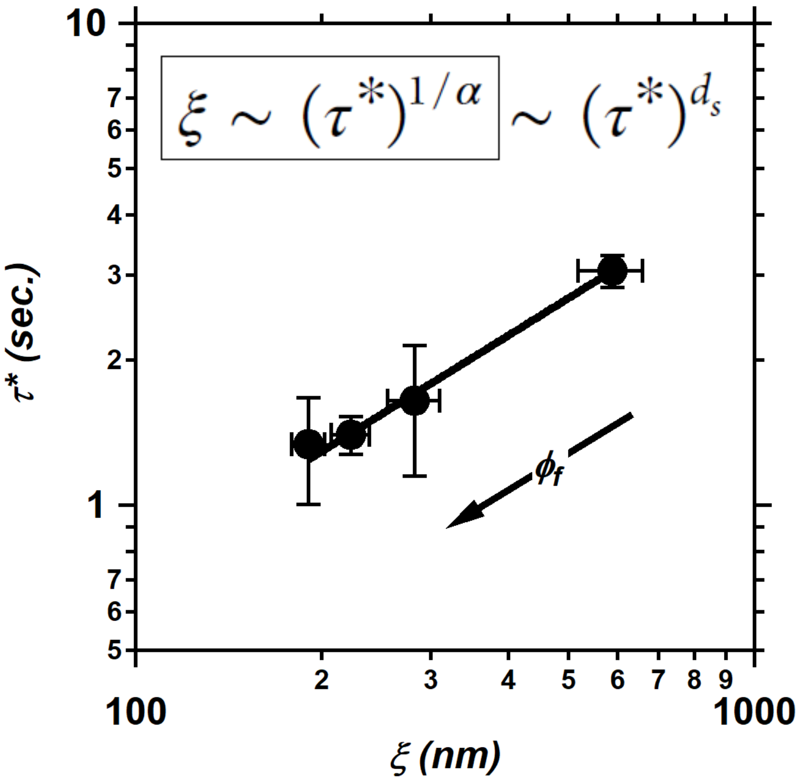
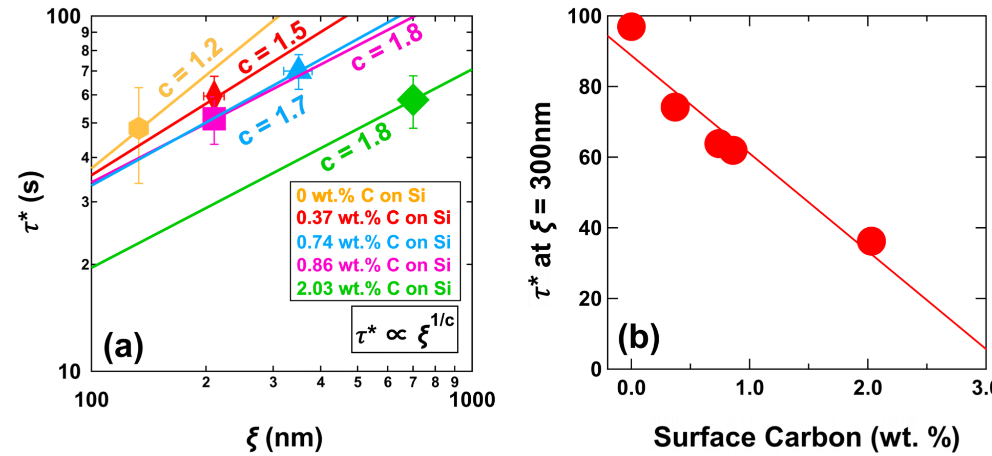
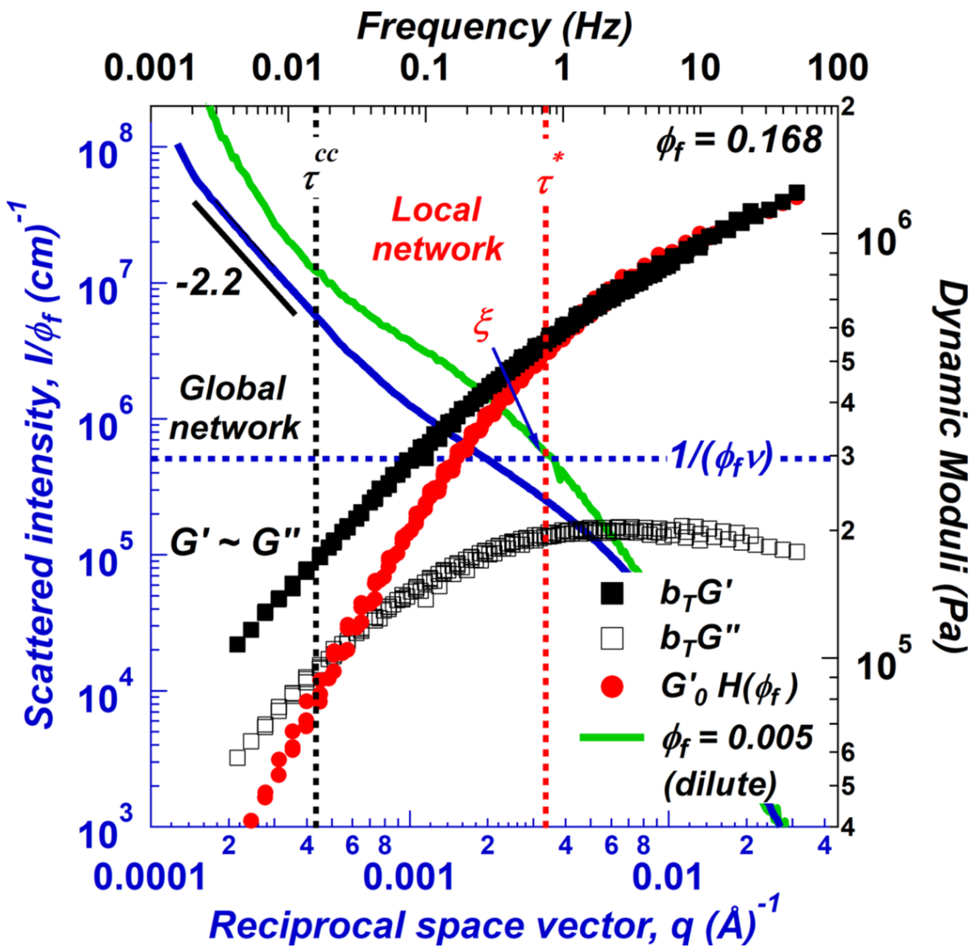


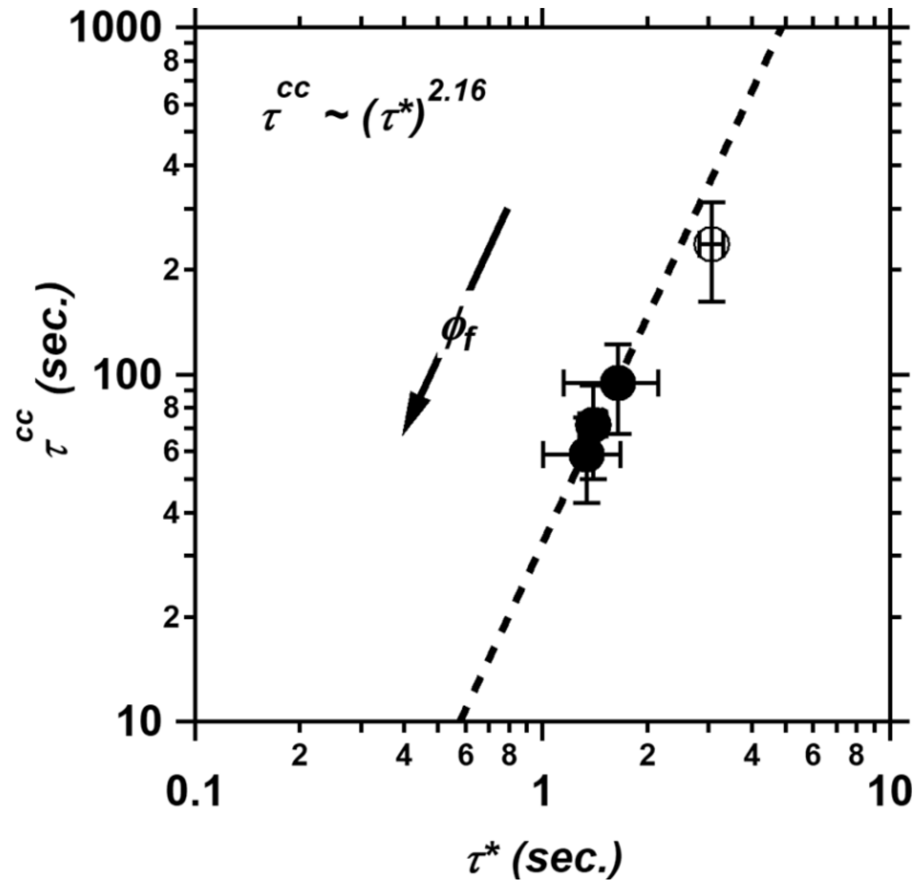


Okoli, U.; Rishi, K.; Beaucage, G.; Kammler, H. K.; McGlasson, A.; Michael, C.; Narayanan, V.; Grammens, J. *Dispersion and Dynamic Response for Flame-Synthesized and Chemically Modified Pyrogenic Silica in Rubber Nanocomposites*; submitted 2022. *Composites Sci. & Tech.*

Nanoscale control over hierarchical response

Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.





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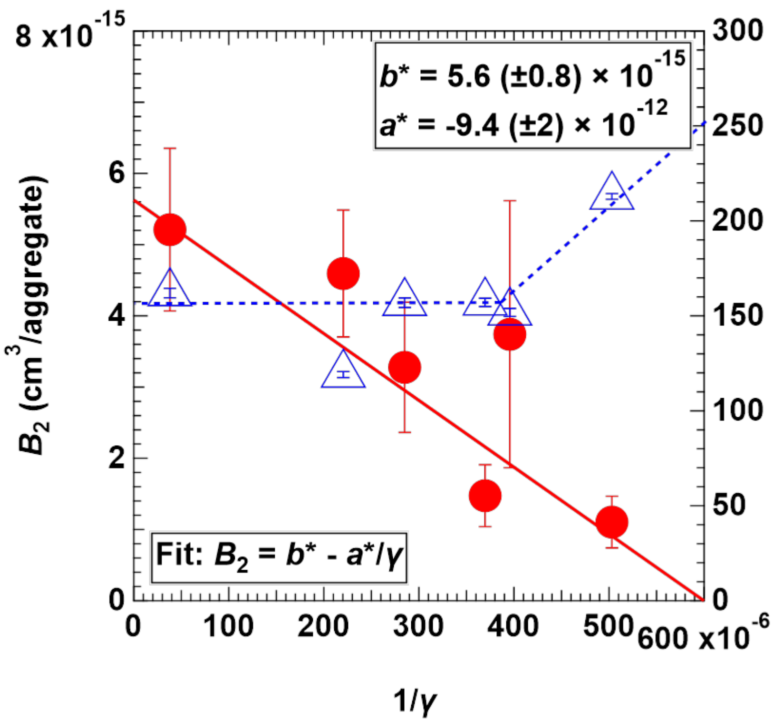
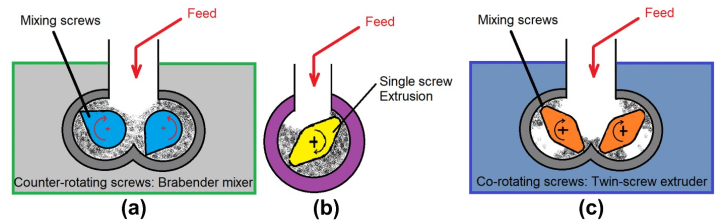
Macroscopic network dynamics is related to nanoscale clusters through the network d_f

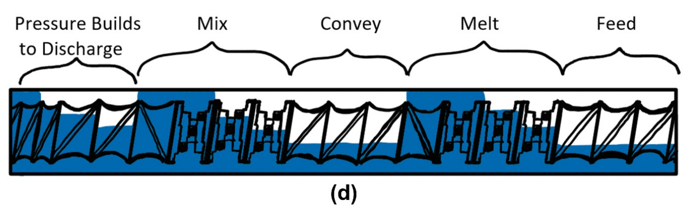
Mixing Geometry and Shear Rate => Hierarchical Emergence

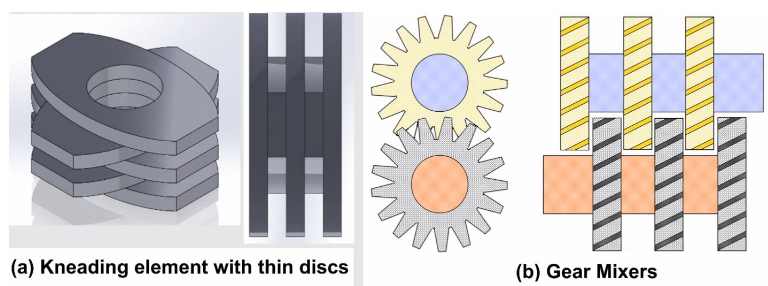
$$B_2(t) = K\left(b^* - \frac{a^*}{\gamma}\right)$$

Carbon Black in Polystyrene









Veigel D., Rishi K., BeaucageG., Galloway J., Campanelli1 H., Ilavsky J., Kuzmenko I., Fickenscher M., Okoli U *Nanocomposite dispersion in melt mixers* in preparation for *Polymer* (2022).

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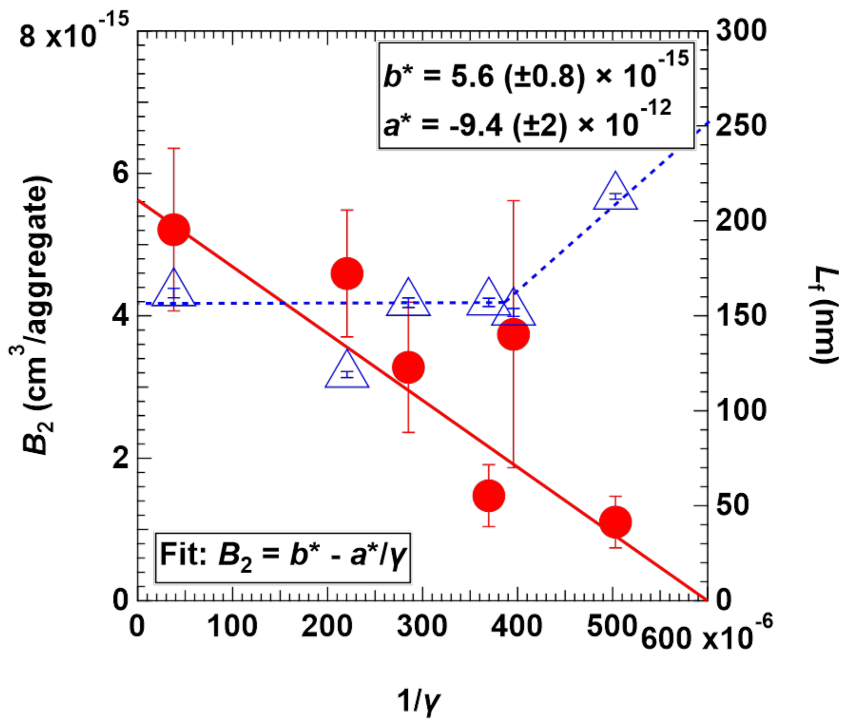
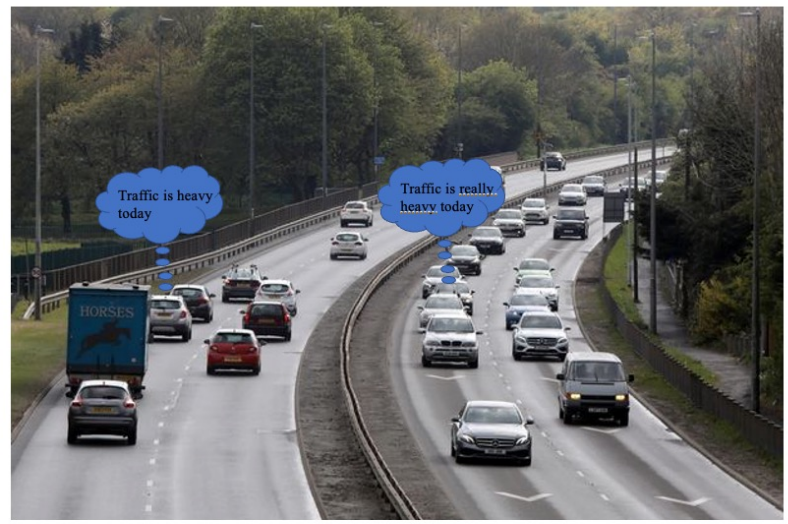
Mixing Geometry and Shear Rate => Hierarchical Emergence

Carbon Black in Polystyrene



Veigel D., Rishi K., Beaucage G., Galloway J., Campanelli1 H., Ilavsky J., Kuzmenko I., Fickenscher M., Okoli U *Nanocomposite dispersion in melt mixers* in preparation (2022).

Clustering can lead to locally higher concentrations



B_2 within the cluster how are the aggregates distributed (larger is better distributed, 0 is unmixed).
L_f how the clusters are distributed between clusters (smaller is better distributed).

Nano-Maufacturing

One View of NM

- Proposition: **The Challenge is to Build Hierarchy**
- The formation of **bulk network** on the cm scale is dictated by the **nature of clustered aggregates** and the **surface chemistry** and **particle size**, and **mixing kinetics**
- The point of **particle modification** is to **control immiscibility and hierarchical emergence** not to enhance miscibility
- **Hierarchical structure** is associated with **hierarchical dynamic response**

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Greg Beaucage, Professor of Chemical and Materials Engineering (beaucag@uc.edu or **gbeaucage@gmail.com**)
Kabir Rishi, CDC/NIOSH
Department of Chemical and Materials Engineering, University of Cincinnati

Alex McGlasson (UMass), Vikram Kuppa (UDRI), Andrew Mulderig (Omya), Vishak Narayanan, Min Rackaitis (Bridgestone), Jan Ilavsky (Argonne), Karsten Vogtt, Hanqiu Jiang (CIP), Jan Jin, Jay Kim (Bridgestone), Lisa Clapp (Sun), Don Henderson (Sun), Danielle Veigel, Jeff Galloway (KraussMaffei), Hanna Campanelli

3660094 - Quantification of nano-dispersion in polymer nanocomposites: A thermodynamic analogy 03:40pm - 04:00pm USA / Canada - Eastern - March 22, 2022 | Location: Virtual 21
Gregory Beaucage, Presenter; **Kabir Rishi**
Division: [PMSE] Division of Polymeric Materials Science and Engineering
Session Type: Oral - Virtual

Nanoparticles in solution are characterized by colloidal thermodynamics such as the second virial coefficient and Debye charge screening. We have found that this approach can be adapted to kinetic mixing in Banbury mixers, twin screw and single screw extruders. An analogy is made between thermal dispersion and kinetic dispersion. This allows adaptation of the van der Waals model to describe nanoscale dispersion in terms of enthalpic interactions and excluded volume. Enthalpic interactions can be in the form of specific interactions that lead to correlated nanoparticles or mean field interactions that result in disordered particles. Specific Coulombic interactions display Debye screening that can result in a critical concentration where a transition between specific and mean field behavior is observed. In many situations, such as elastomer reinforcement, nano-scale dispersion is not optimal since agglomeration on the nano-scale can enable the formation of a network on macroscopic scales assocated with properties such as tear resistance.

Quantification of nano-dispersion in polymer nanocomposites: A thermodynamic analogy

Greg Beaucage, Professor of Chemical and Materials Engineering

Kabir Rishi, NIOSH Research Laboratory, Cincinnati Ohio

Department of Materials Science & Engineering, University of Cincinnati

Hierarchical emergent structure in commercial colloidal and polymeric systems

Greg Beaucage, Professor of Chemical and Materials Engineering
Kabir Rishi, CDC/NIOSH
Department of Materials Science & Engineering, University of Cincinnati

One View of NM:

- Proposition: Nano-Manufacturing Involves Hierarchy, **The Challenge is to Build Hierarchy**

- The formation of **bulk network** on the cm scale is dictated by the **nature of clustered aggregates** and the **surface chemistry** and **particle size**, and **mixing kinetics**

- The point of **particle modification** is to **control immiscibility and hierarchical emergence** not to enhance miscibility

- The **hierarchical structure** is associated with **hierarchical dynamic response**