Hierarchical emergent structure in commercial colloidal and polymeric systems

11:30am - 11:45am USA / Canada - Eastern - August 24, 2021 | Room: Zoom Room 21
Gregory Beaucage, Presenter; Kabir Rishi
Division: [PMSE] Division of Polymeric Materials Science and Engineering
Session Type: Oral - Virtual

In commercial products additives with limited or no miscibility with a base resin or solvent are often encountered. Through manipulation of interfacial agents and kinetic milling, mixing or extrusion, nano- to colloidal-scale additives assemble into micron- to millimeter-scale structures that can gel or produce desired optical scattering, electrical conduction, mechanical reinforcement, and engineered rheology. These emergent multi-hierarchical networks are important in many applications. We have studied several examples of these systems. Generally they can be categorized into thermally dispersed and mechanically dispersed systems. **Thermal dispersion**: Inks containing organic pigments are miscibilized in water using non-ionic surfactants. Depending on the phase behavior of these surfactants and the milling history, the primary structure, aggregate structure and macroscopic network structure can be tuned. In a printer the complex structure can be subject to shear that further influences the structure. Finally, as concentration increases with drying a complex, robust network on the micron scale, fused with binder in some cases, can scatter light and give mechanical strength to the dried film. Although the initial, shelf-stable system is thermally dispersed, a complex interplay between kinetic and thermodynamic features govern the resulting film. **Kinetic dispersion**: For reinforced elastomers and many filled polymers such as carbon black filled polyethylene for UV protection or polymer solid electrolytes the additives are inherently immiscible, yet it is desired to produce a macroscopic network from nanoscale structures for mechanical strength, electrical conductivity and optical and UV scattering. In these systems we can make a crude approximation that the accumulated strain shows similarity to temperature in thermally dispersed systems in that it leads to random dispersion of nano- or colloidal particles. We can make some gross approximations using what is known about thermally dispersed colloidal systems to understand the impact of excluded volume and interaction energies in the context of a kinetic pseudo-temperature. This approach has proven fruitful in understanding dispersion with some nuances. For instance, in

Hierarchical emergent structure in commercial colloidal and polymeric systems

Greg Beaucage, Professor of Chemical and Materials Engineering

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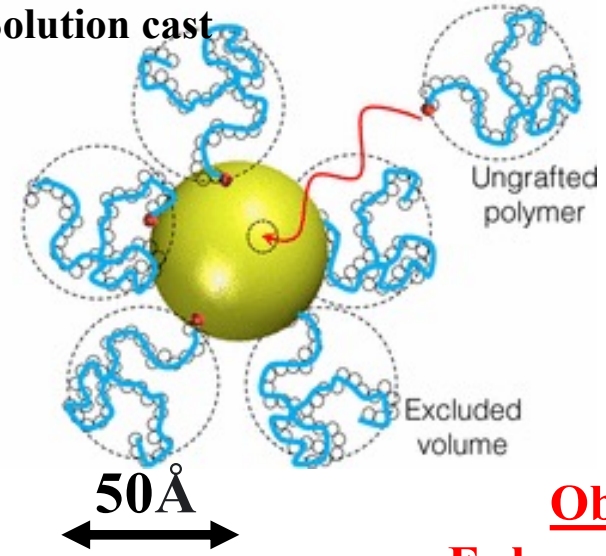
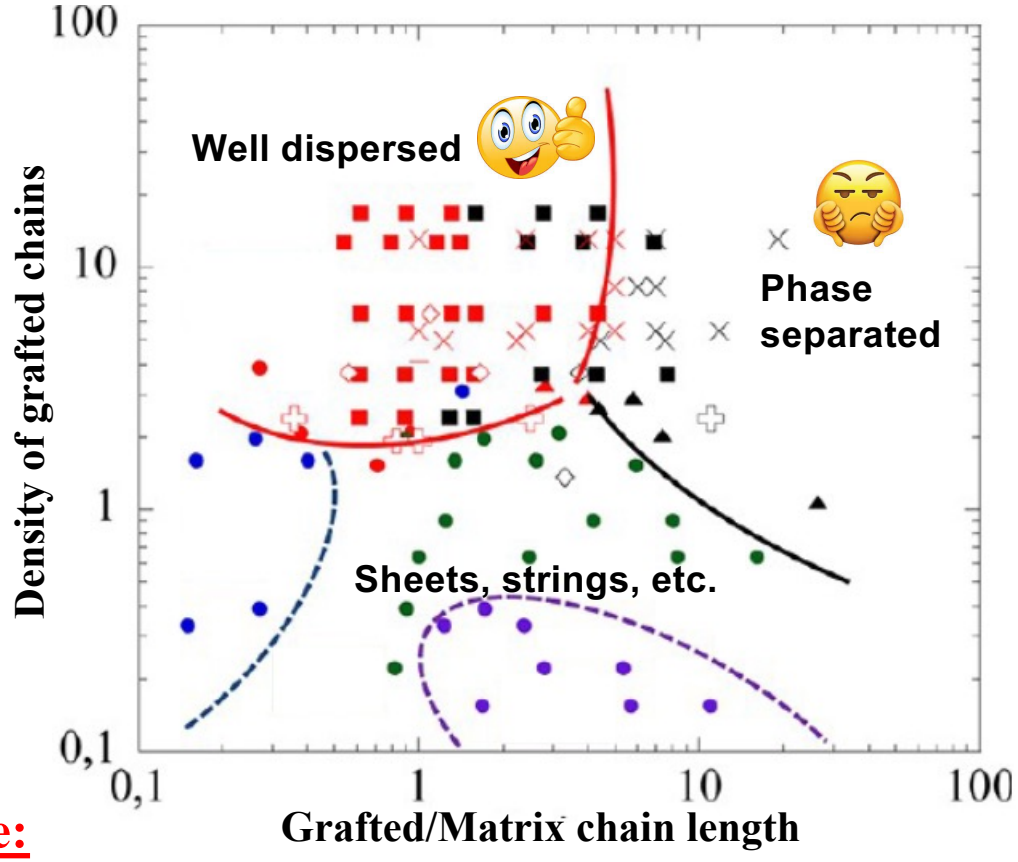
Current state-of-the-art nanocomposite

Monodisperse colloidal particles

Colloidal Solution cast

Thermally Dispersed





Objective:
Enhance miscibility

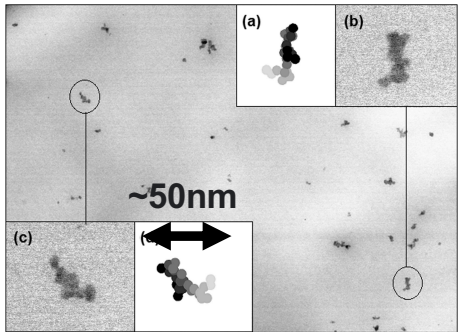
Kumar, S.K., Jouault, N., Benicewicz, B. and Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules*, *46*(9), pp.3199-3214.
Kumar, S.K., Benicewicz, B.C., Vaia, R.A. and Winey, K.I., 2017. 50th anniversary perspective: are polymer nanocomposites practical for applications?. *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

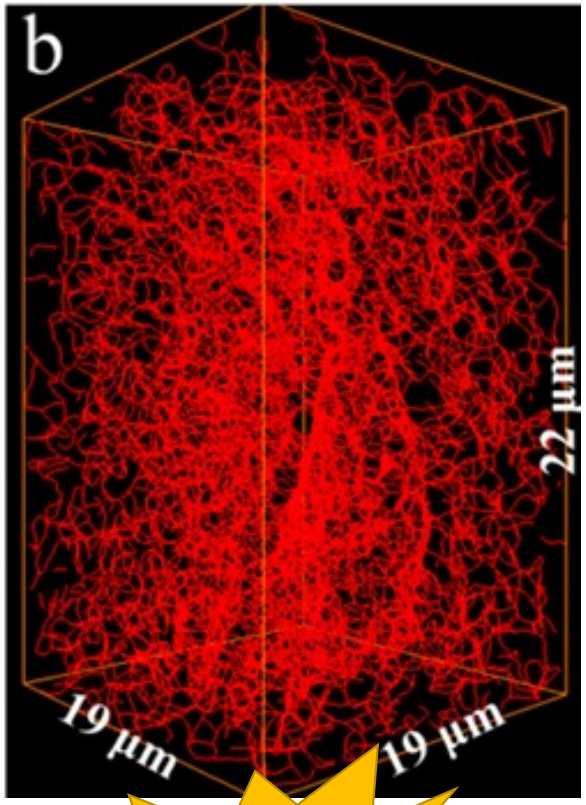
Polydisperse aggregates

Processed under shear

Kinetically mixed **immiscible**



Objective:
Tear resistance
Static charge dissipation

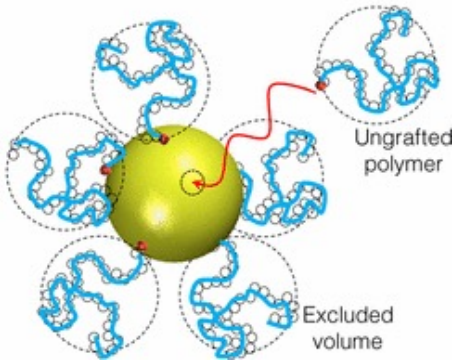


Why/how do added nanoparticles impact structures 100-1,000 times larger?

1,000 x larger

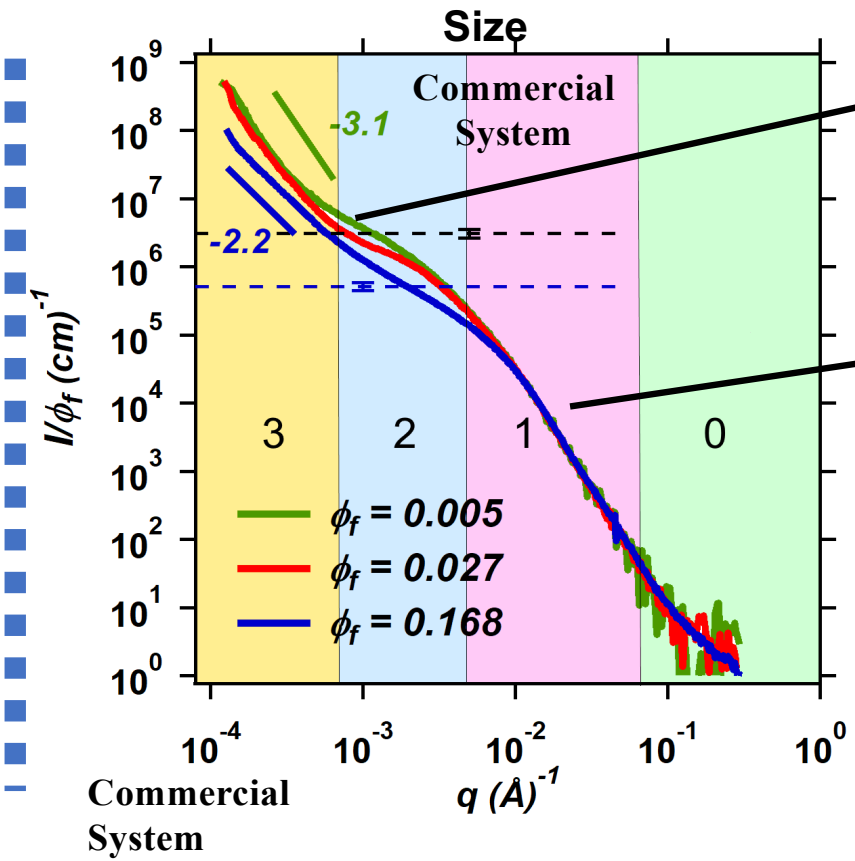
Song, L; Wang, Z; Tang, X.; Chen, L.; Chen, P.; Yuan, Q.; **Li, L.** Visualizing the Toughening Mechanism of Nanofiller with 3D X-ray Nano-CT: Stress-Induced Phase Separation of Silica Nanofiller and Silicone Polymer Double Networks Macromolecules 50 7249-7257 (2017).

Multiscale Hierarchical Structures

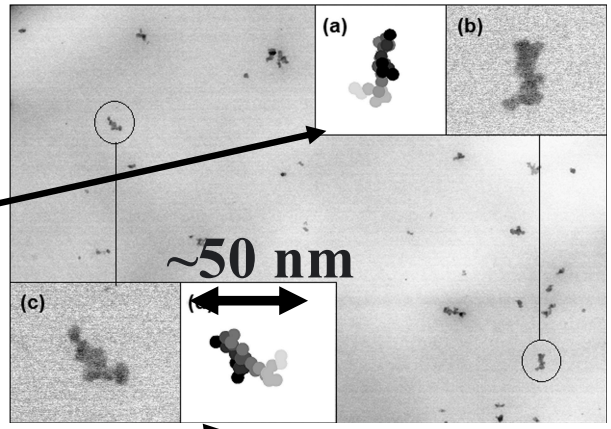


50Å

State of the Art Model System



Commercial System



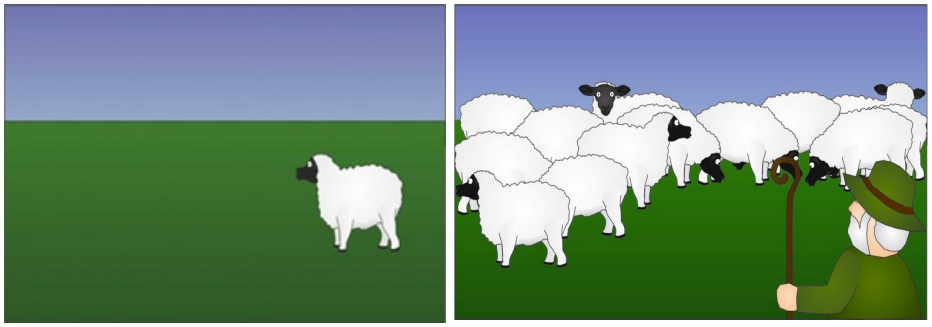
Aggregates of primary particles

One size scale vs. multiple hierarchical size scales

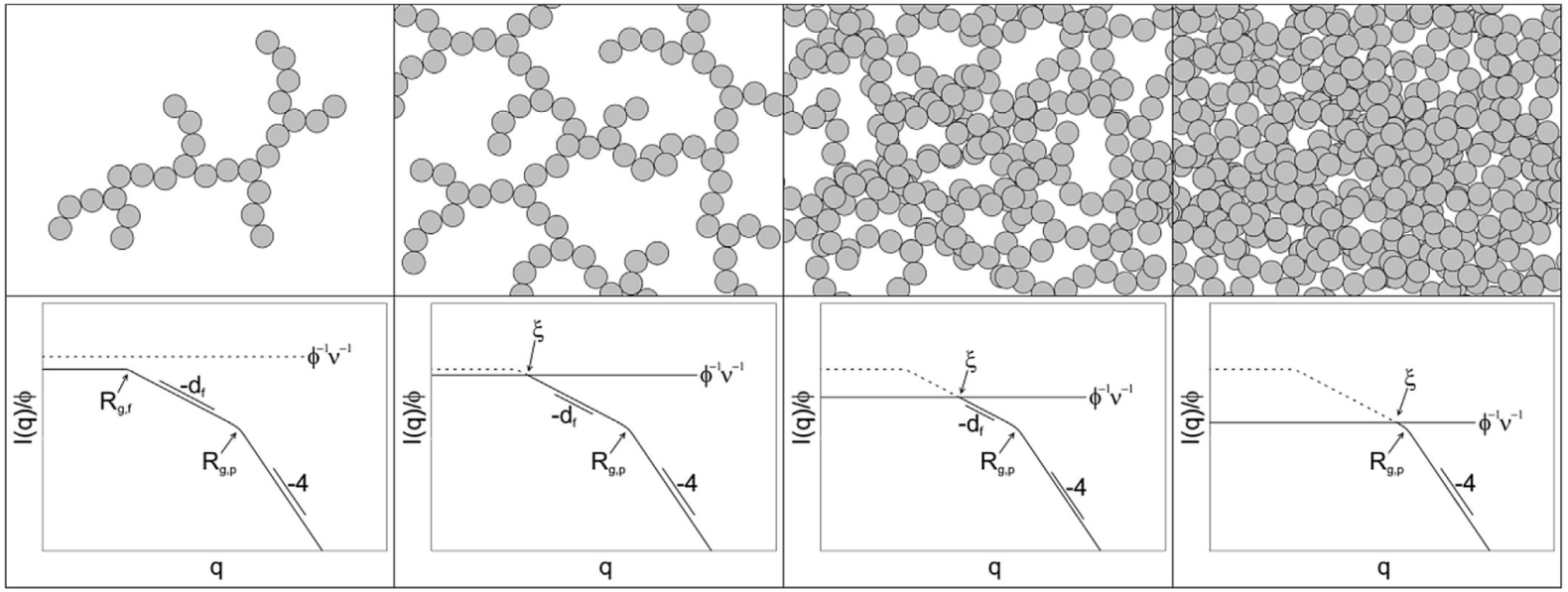
Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

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 from scattering



Quantitative measure of nano-dispersion



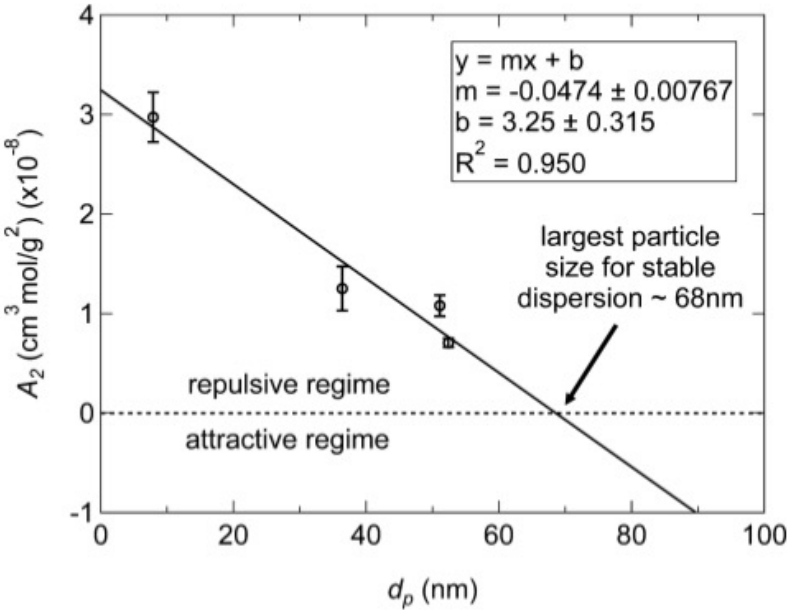
Pedersen, J. S.; Sommer, C. Temperature Dependence of the Virial Coefficients and the Chi Parameter in Semi-Dilute Solutions of PEG. In *Scattering Methods and the Properties of Polymer Materials*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2005; pp 70–78.

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.

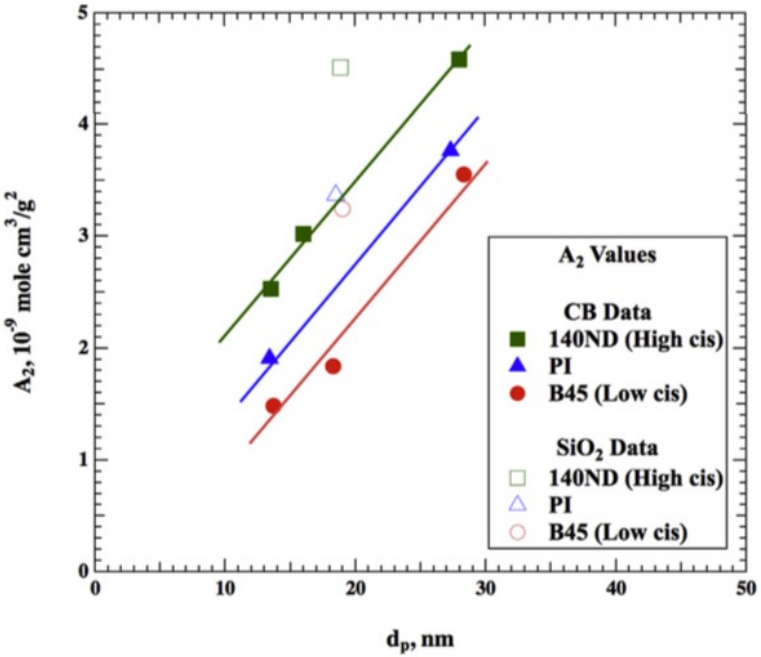
Thermal Dispersion versus Kinetic Dispersion

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

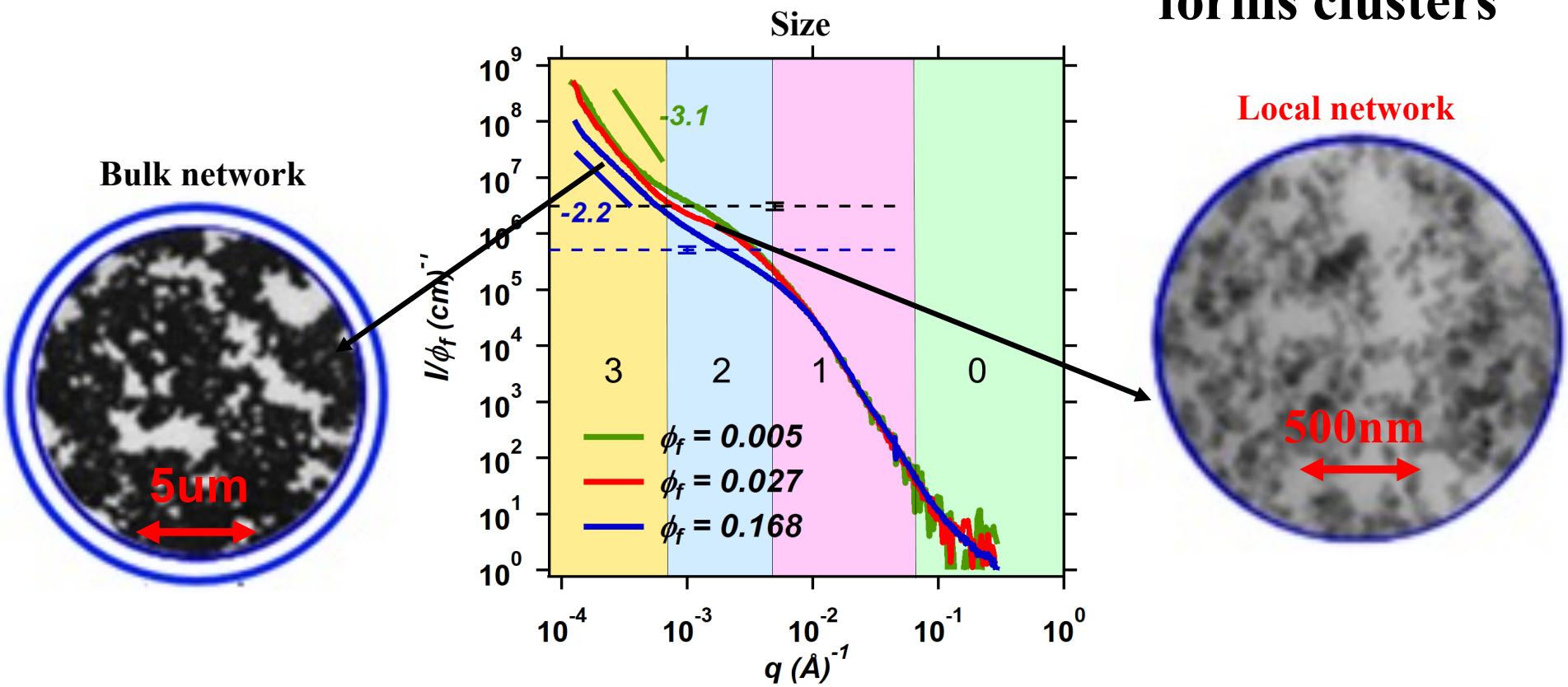
Mulderig, A.; Beaucage, G.; Vogtt, K.; Jiang, H.; Jin, Y.; Clapp, L.; Henderson, D. C. Structural Emergence in Particle Dispersions. *Langmuir* **2017**, *33* (49), 14029–14037.

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

Multiscale Hierarchical Structures

Immiscibility forms clusters



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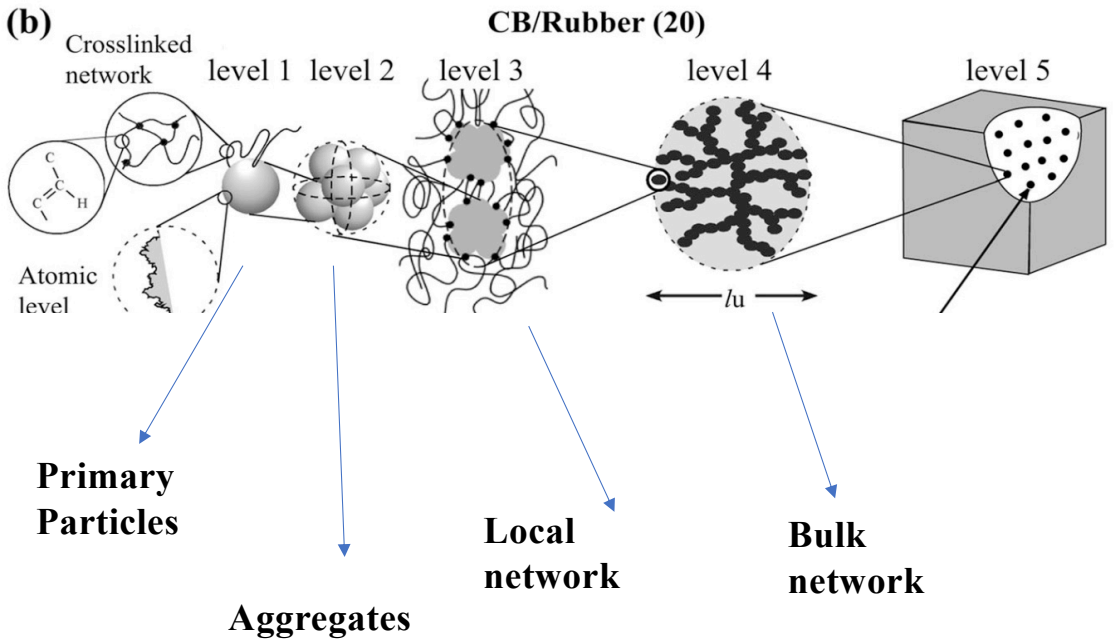
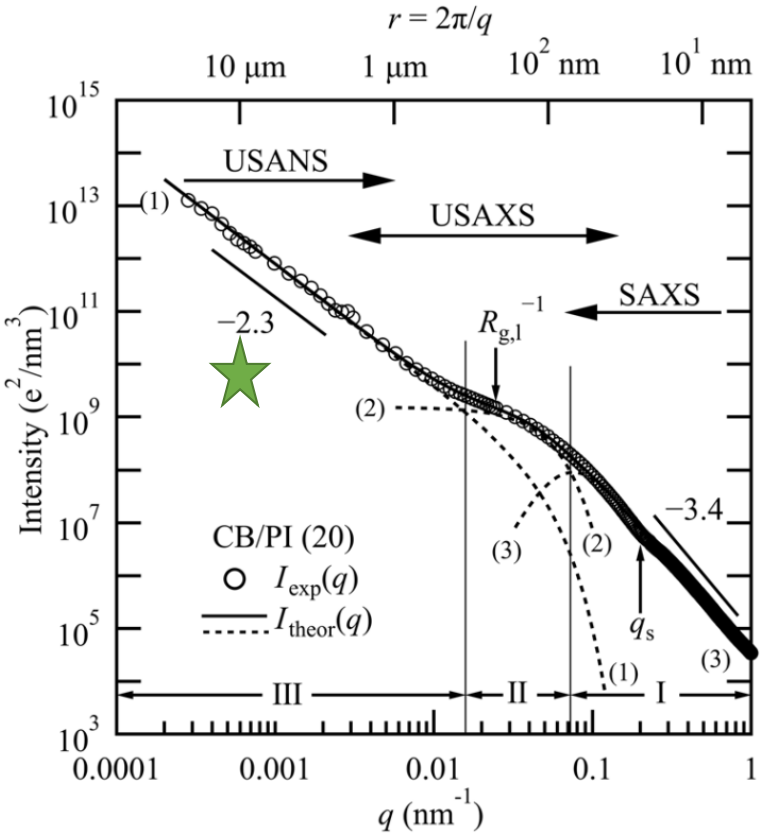
Trappe, V. and Weitz, D.A., 2000. Scaling of the viscoelasticity of weakly attractive particles. *Physical review letters*, *85*(2), p.449.

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.

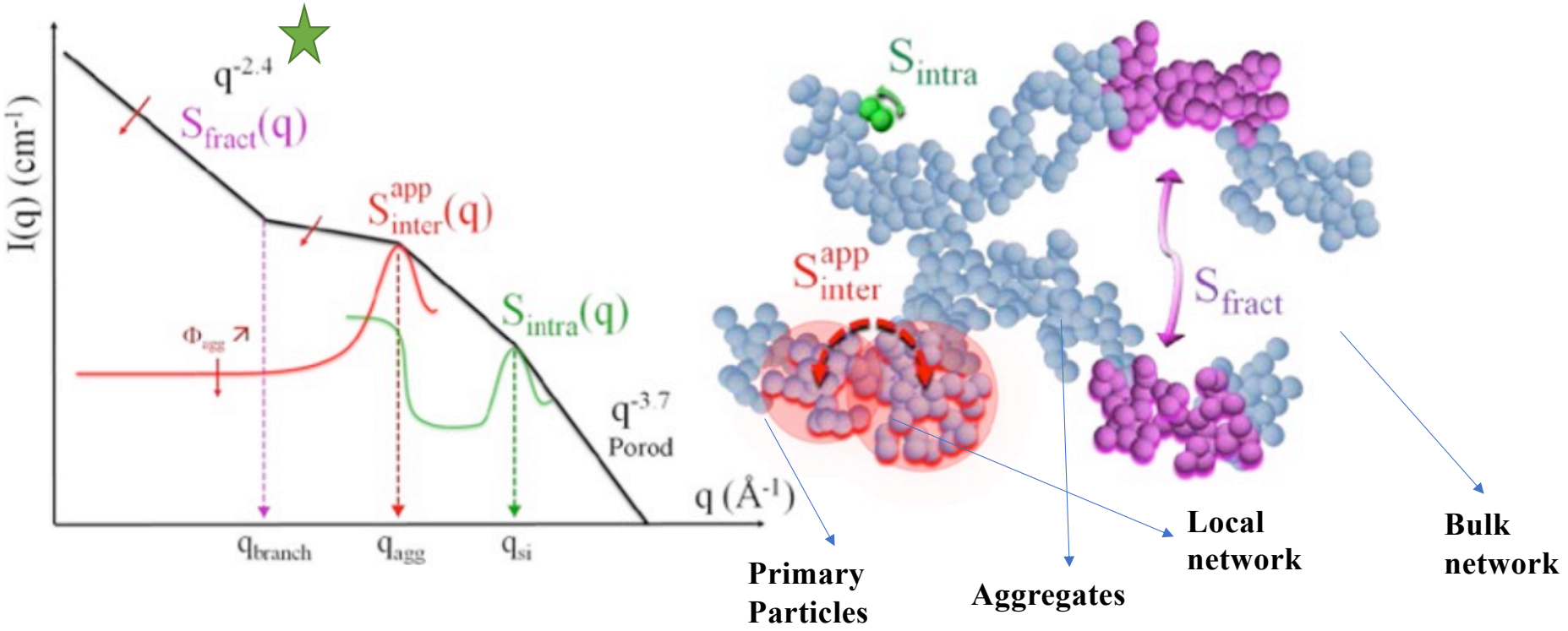
Multiscale Hierarchical Structures





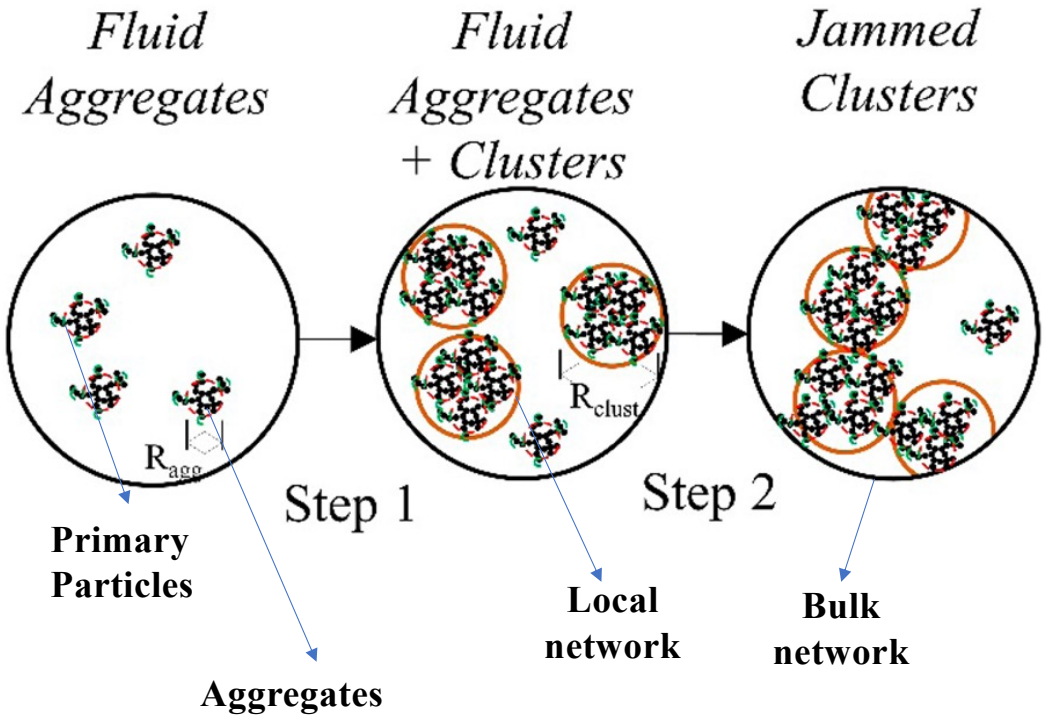
Hashimoto, T., Amino, N., Nishitsuji, S. and Takenaka, M., **2019**. Hierarchically self-organized filler particles in polymers: cascade evolution of dissipative structures to ordered structures. *Polymer Journal*, *51*(2), pp.109-130.

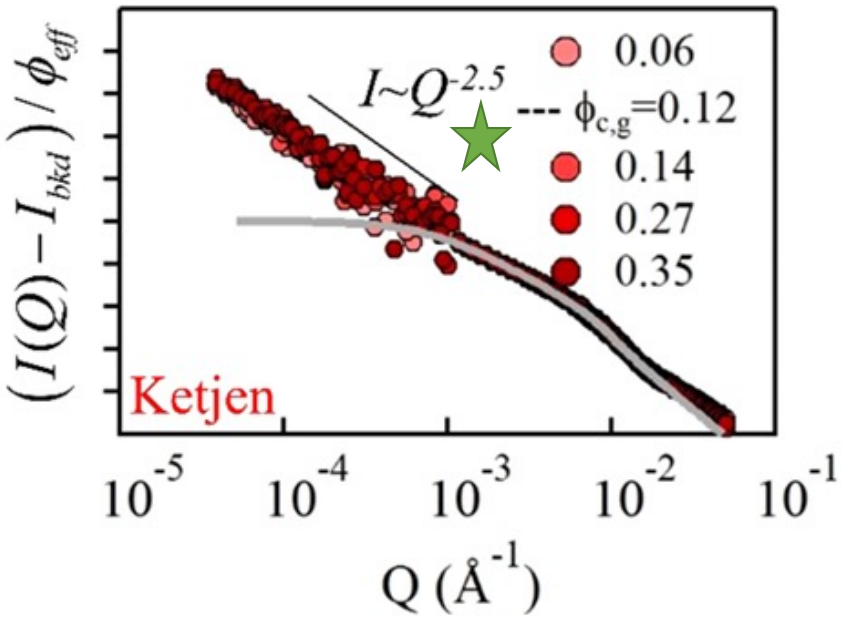
Multiscale Hierarchical Structures



Baeza, G.P., Genix, A.C., Degrandcourt, C., Petitjean, L., Gummel, J., Couty, M. and Oberdisse, J., **2013**. Multiscale filler structure in simplified industrial nanocomposite silica/SBR systems studied by SAXS and TEM. *Macromolecules*, *46*(1), pp.317-329.

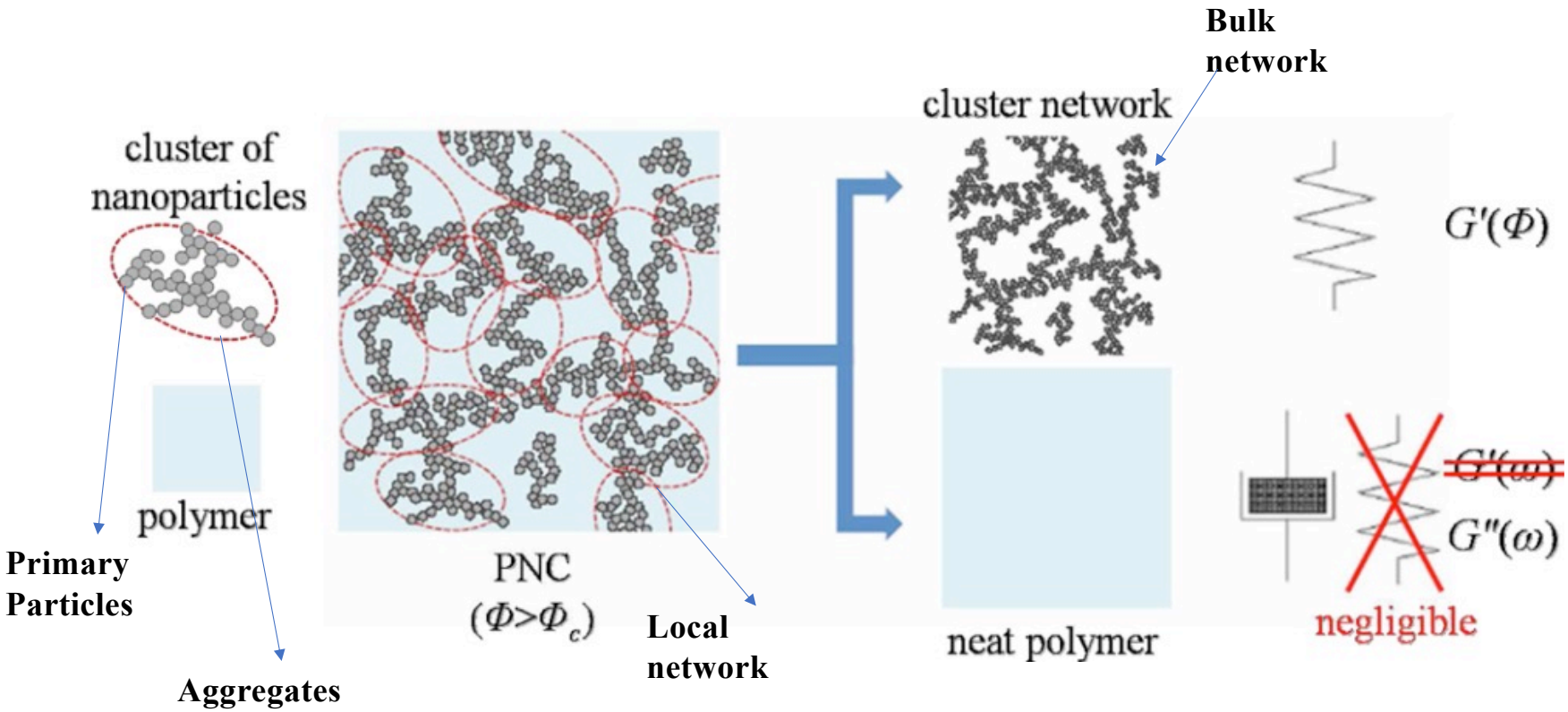
Multiscale Hierarchical Structures





Richards, J.J., Hipp, J.B., Riley, J.K., Wagner, N.J. and Butler, P.D., **2017**. Clustering and percolation in suspensions of carbon black. *Langmuir*, *33*(43), pp.12260-12266.

Multiscale Hierarchical Structures



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.

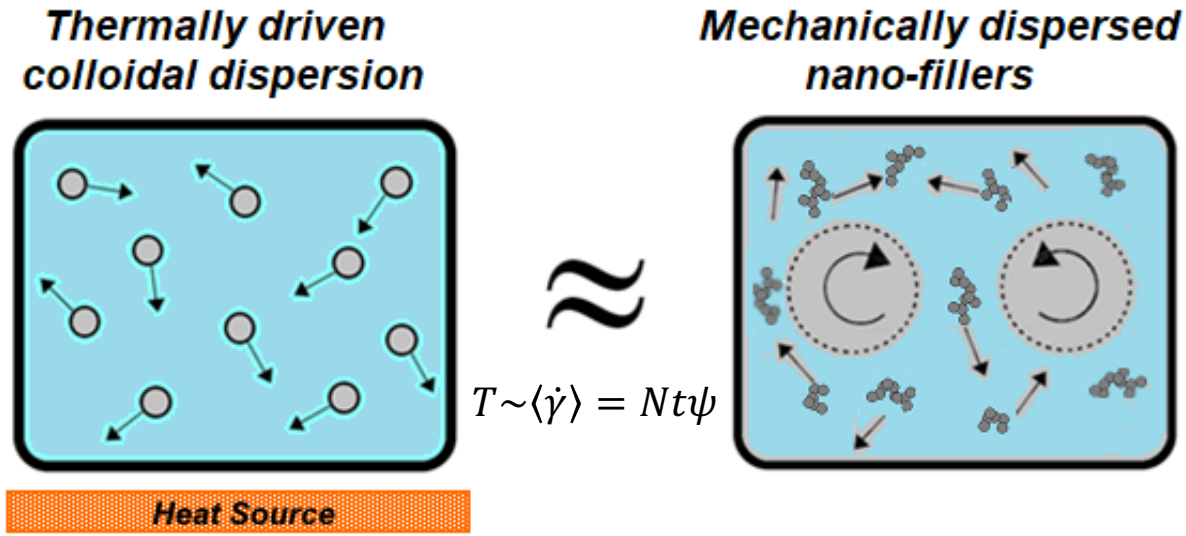
Filippone, G. and Salzano de Luna, M., **2012**. A unifying approach for the linear viscoelasticity of polymer nanocomposites. *Macromolecules*, *45*(21), pp.8853-8860.

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

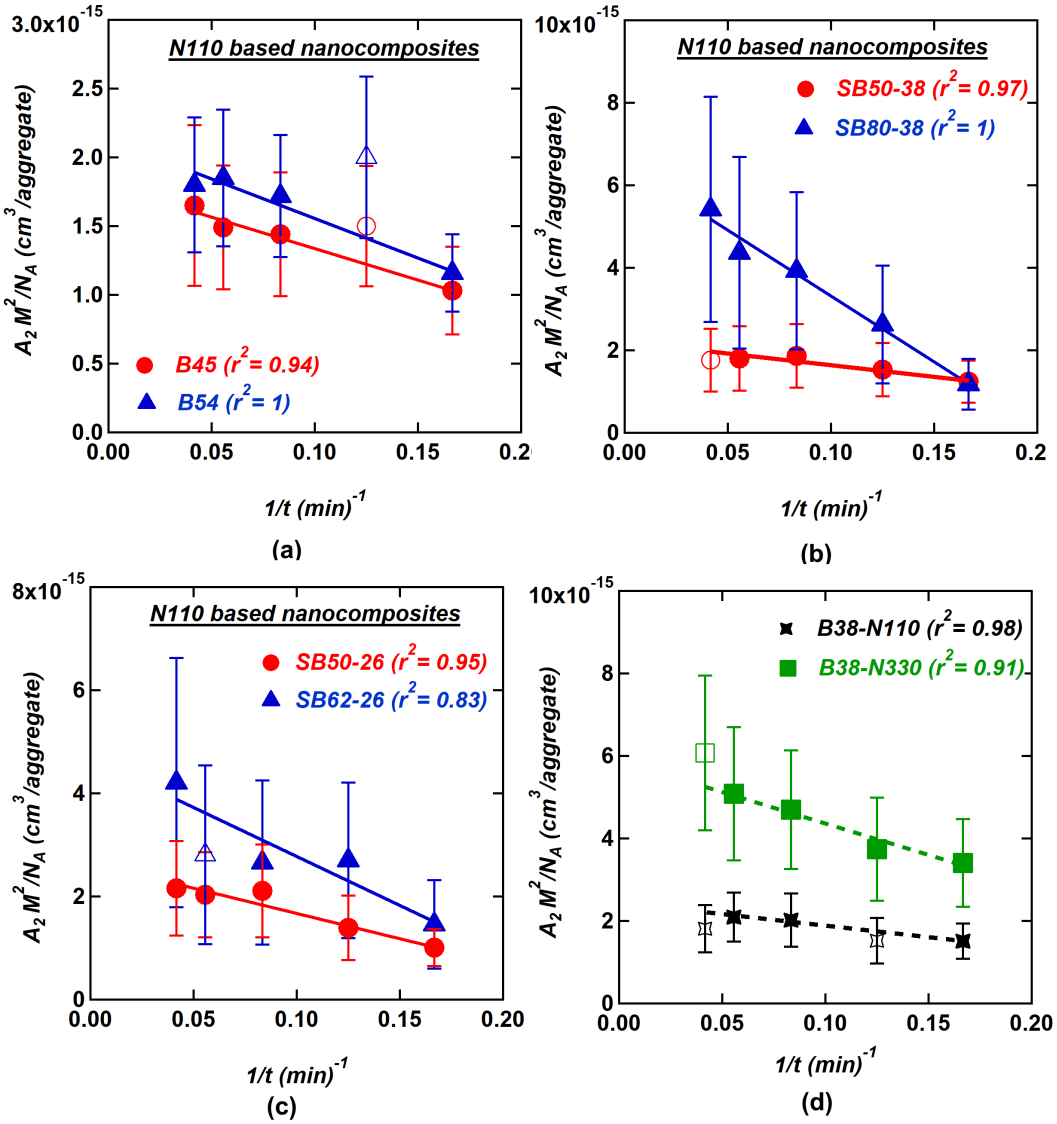


$$T \sim \langle \dot{\gamma} \rangle = Nt\psi$$

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

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

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 (Guildf). **2019**, 175, 272–282.



Van der Waals approach seems viable

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

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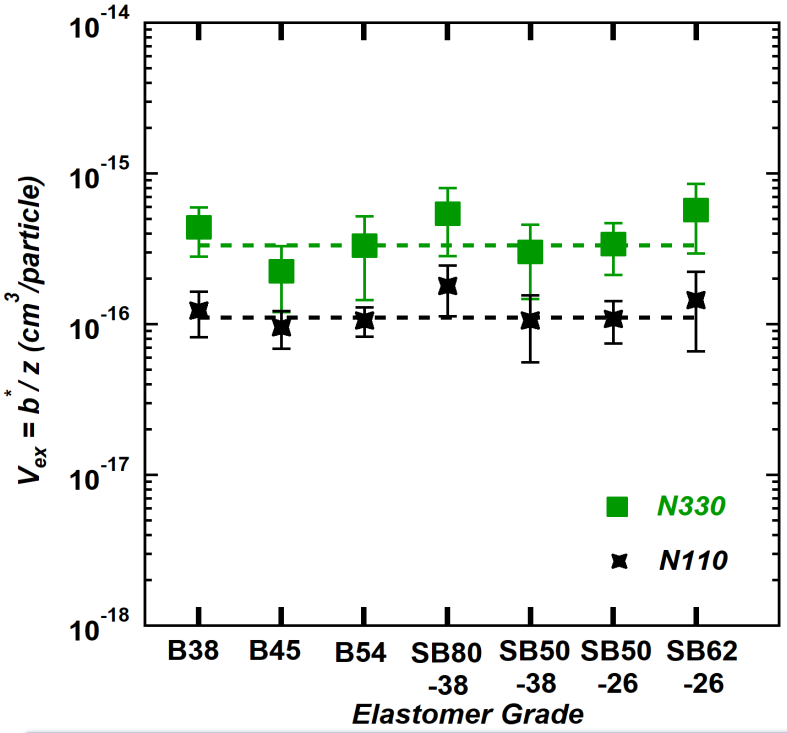
Excluded volume is associated with the occupied volume of an aggregate.

$(d_{p,N330}/d_{p,N110})^3 = 4.2$



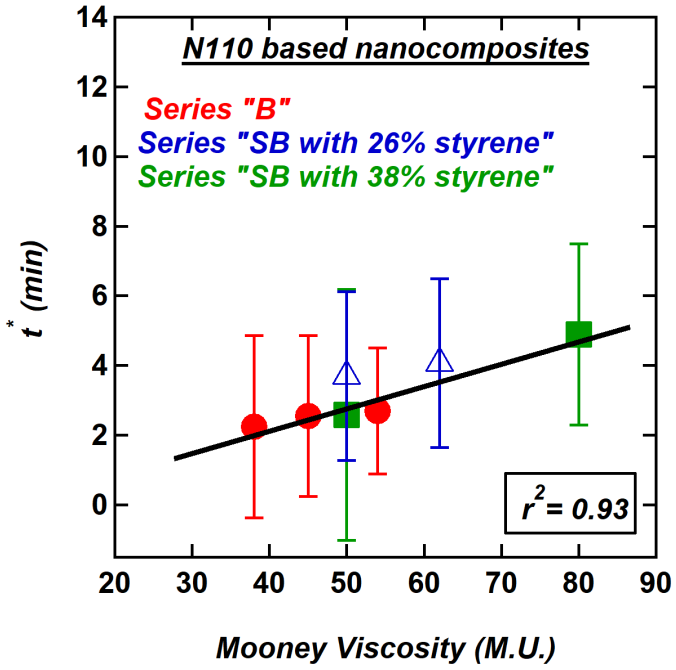
N110	Vulcan 8 (Cabot)	123 m^2/g	25.7 nm
N330	Vulcan 3 (Cabot)	76 m^2/g	41.6 nm

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

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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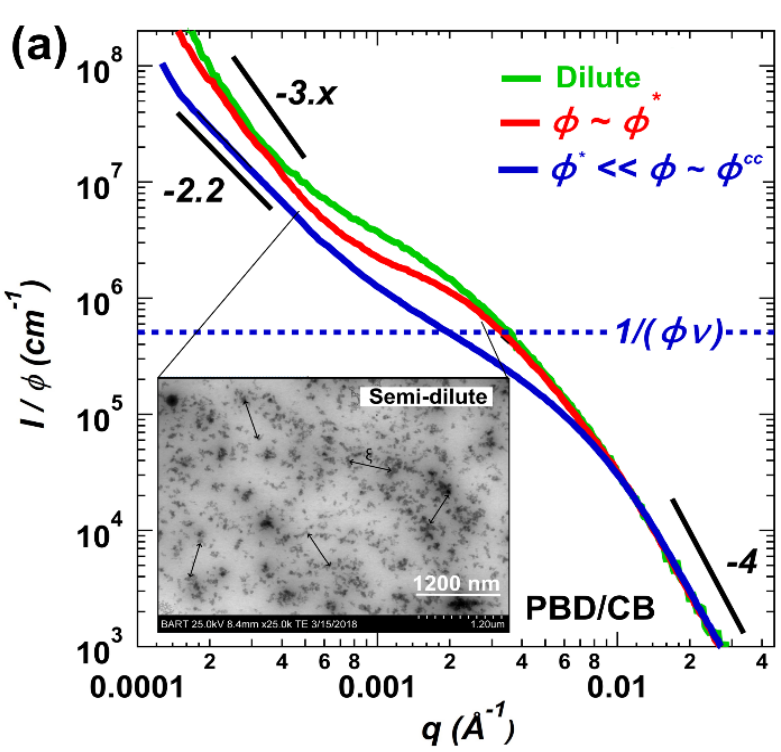
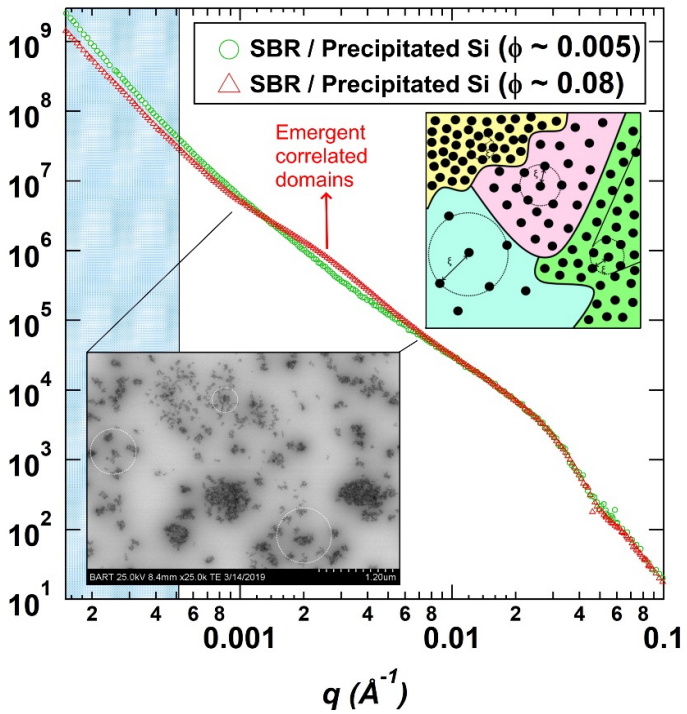
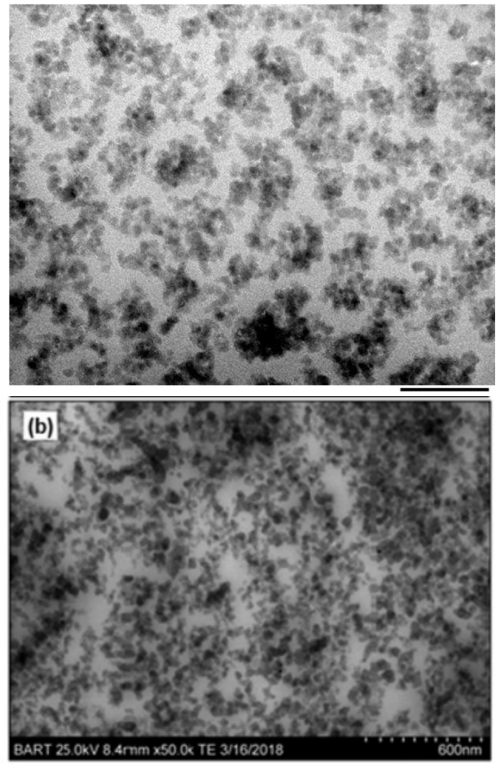
Mean field (CB) and specific interactions (Silica)







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.

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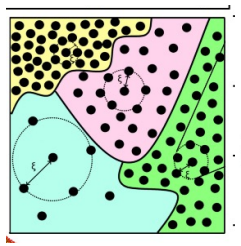
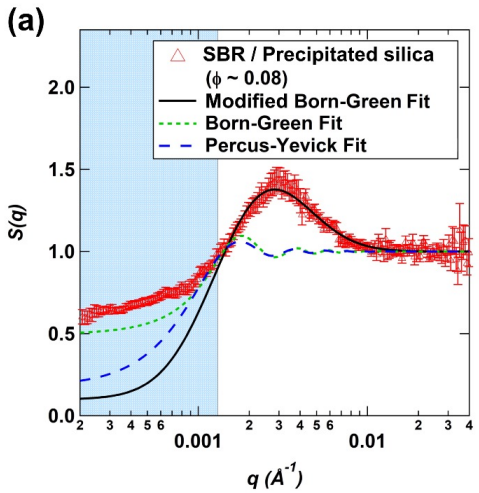
Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

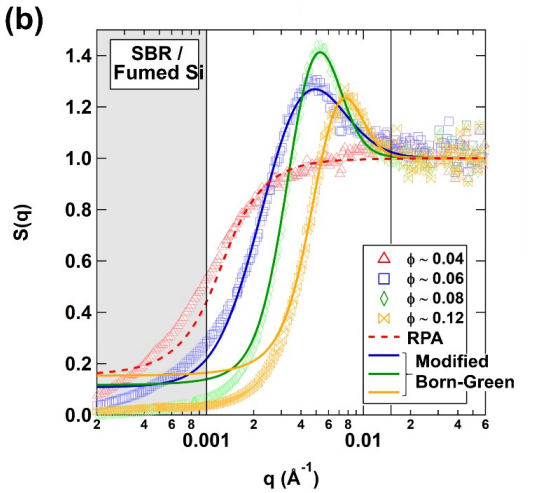
Specific interactions (Silica)

Positive a^* can lead to correlated silica aggregates, New scattering function to fit these curves that/ 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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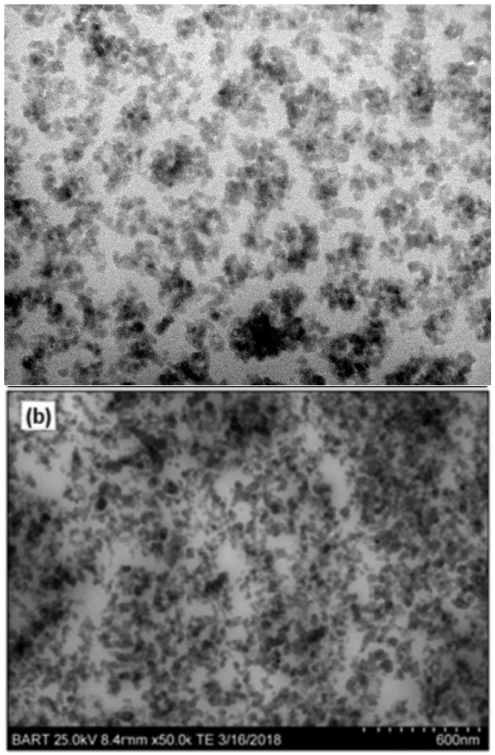

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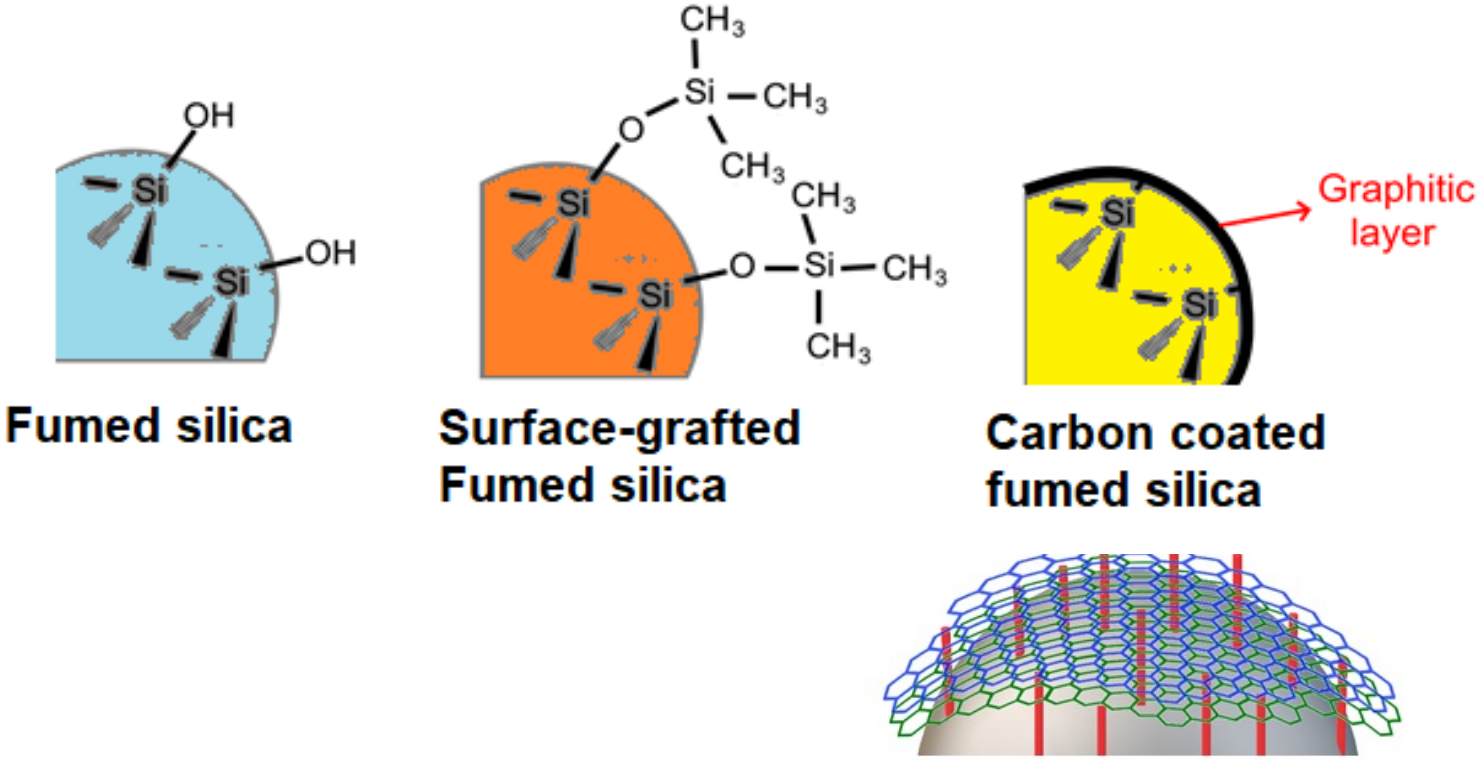
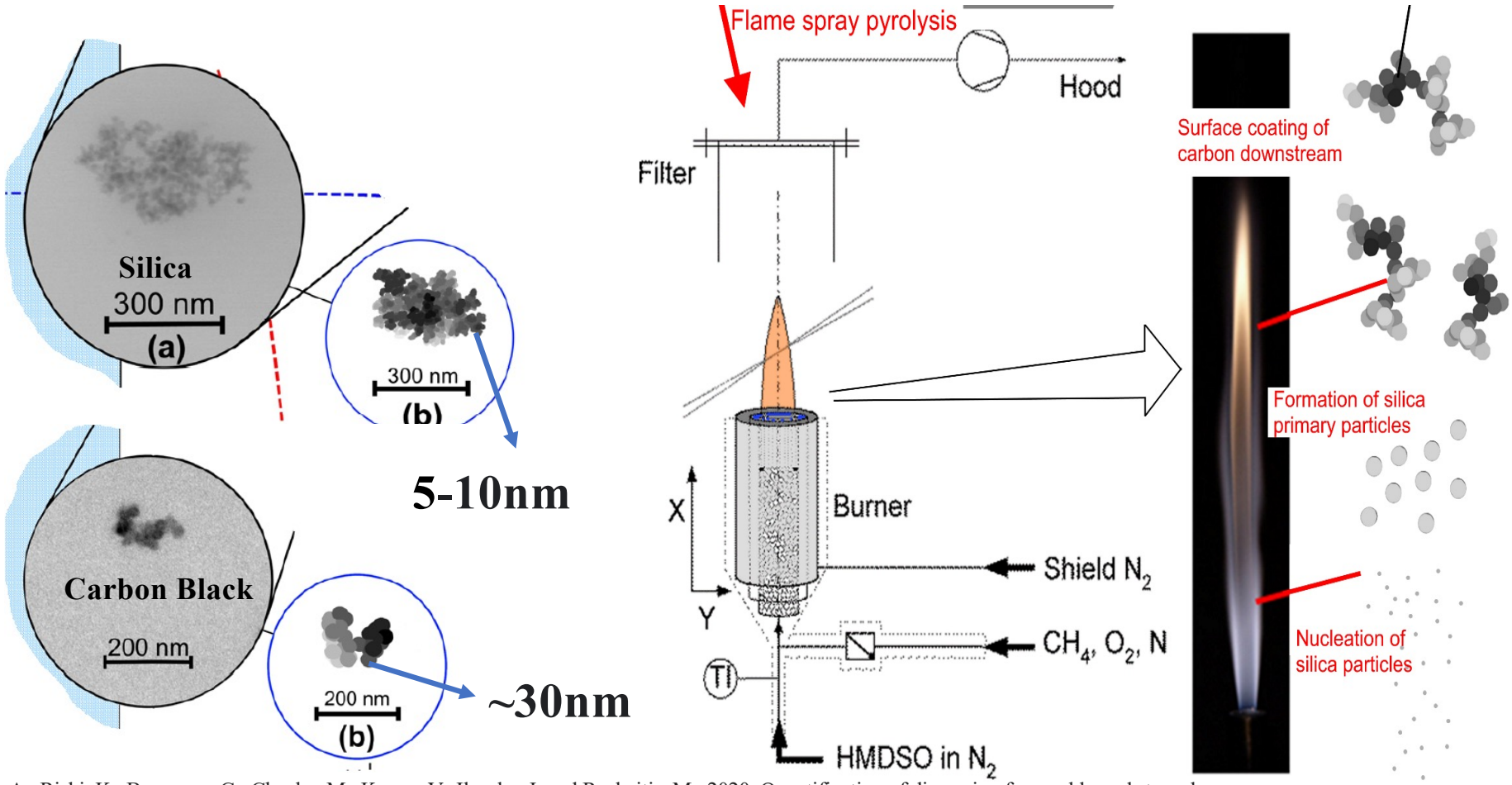
Aggregates to clusters

Control immiscibility 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*; 2021. In preparation.



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Surface Modification for Controlled Immiscibility

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

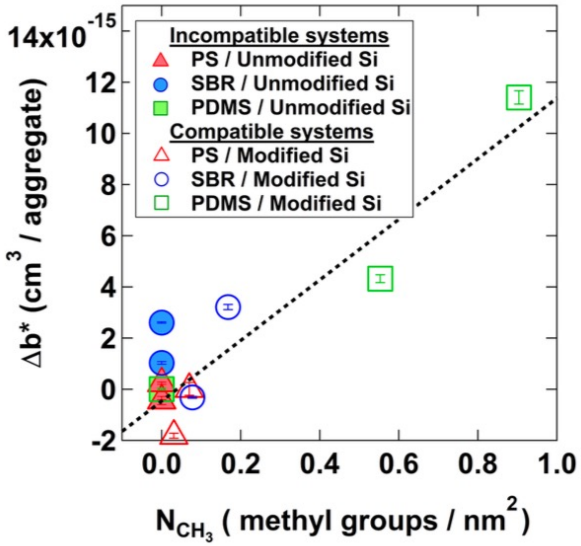
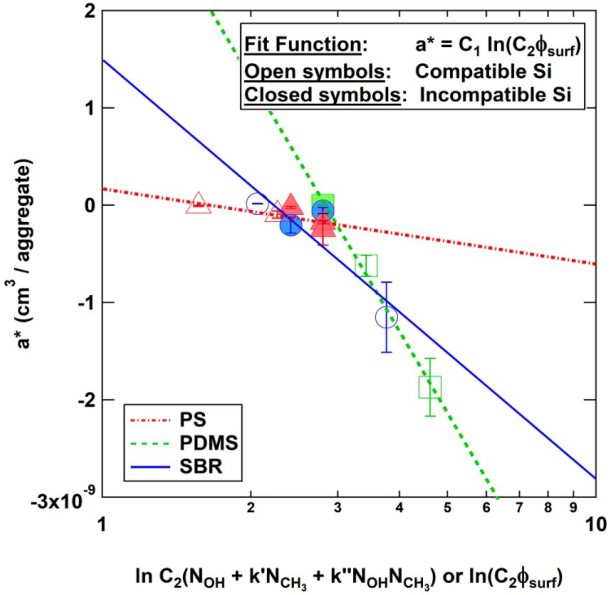
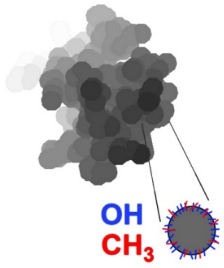


FIG. 11. A plot showing the bound polymer content (Δb^*) determined from the excluded volumes of the filler aggregates before and after dispersion as a function of surface methyl content (N_{CH_3}). The dashed line indicates that Δb^* is proportional to N_{CH_3} determined from FTIR.





$$\exp\left(\Delta G / \gamma\right) = \left(N_{OH} + k'N_{CH_3} + k''N_{OH}N_{CH_3}\right)$$

Adapted from Rishi, K., Pallerla, L., Beaucage, G. & Tang, A. Dispersion of surface-modified, aggregated, fumed silica in polymer nanocomposites. J. Appl. Phys. 127, 174702 (2020).

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

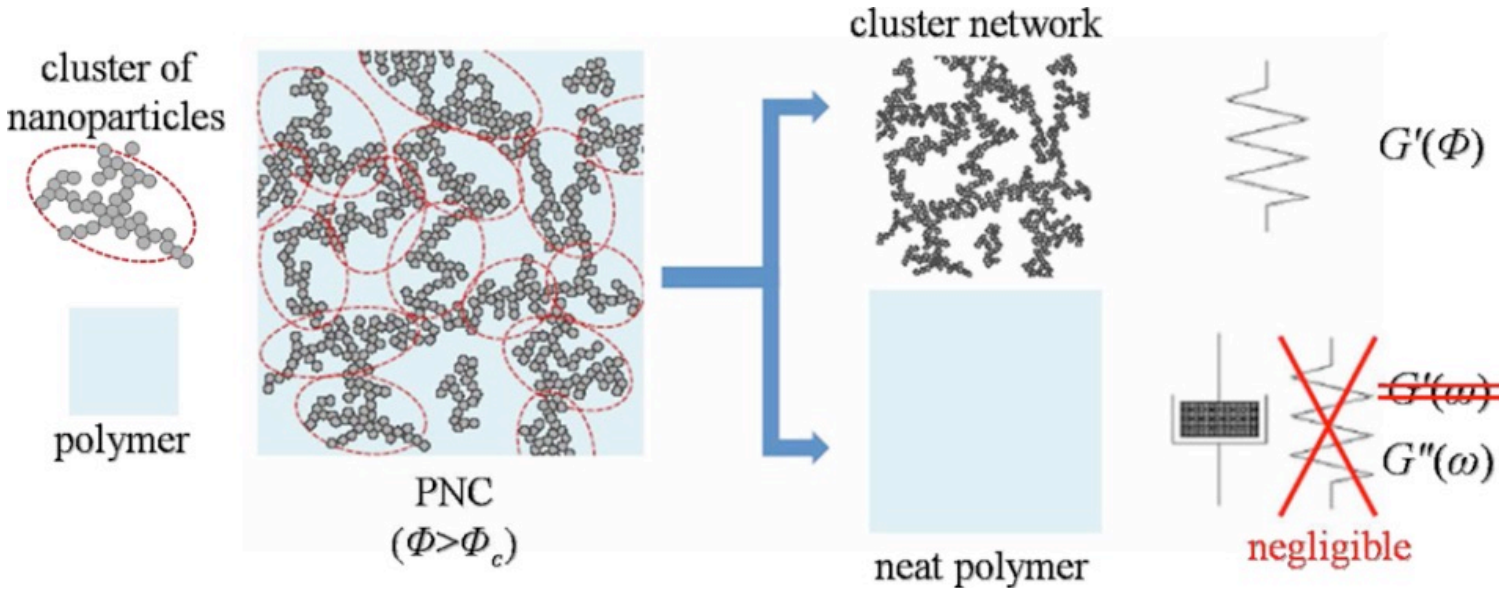
b^* can be calculated as the excluded volume for an aggregate, zV_0, without bound rubber

b^* increases with bound rubber.

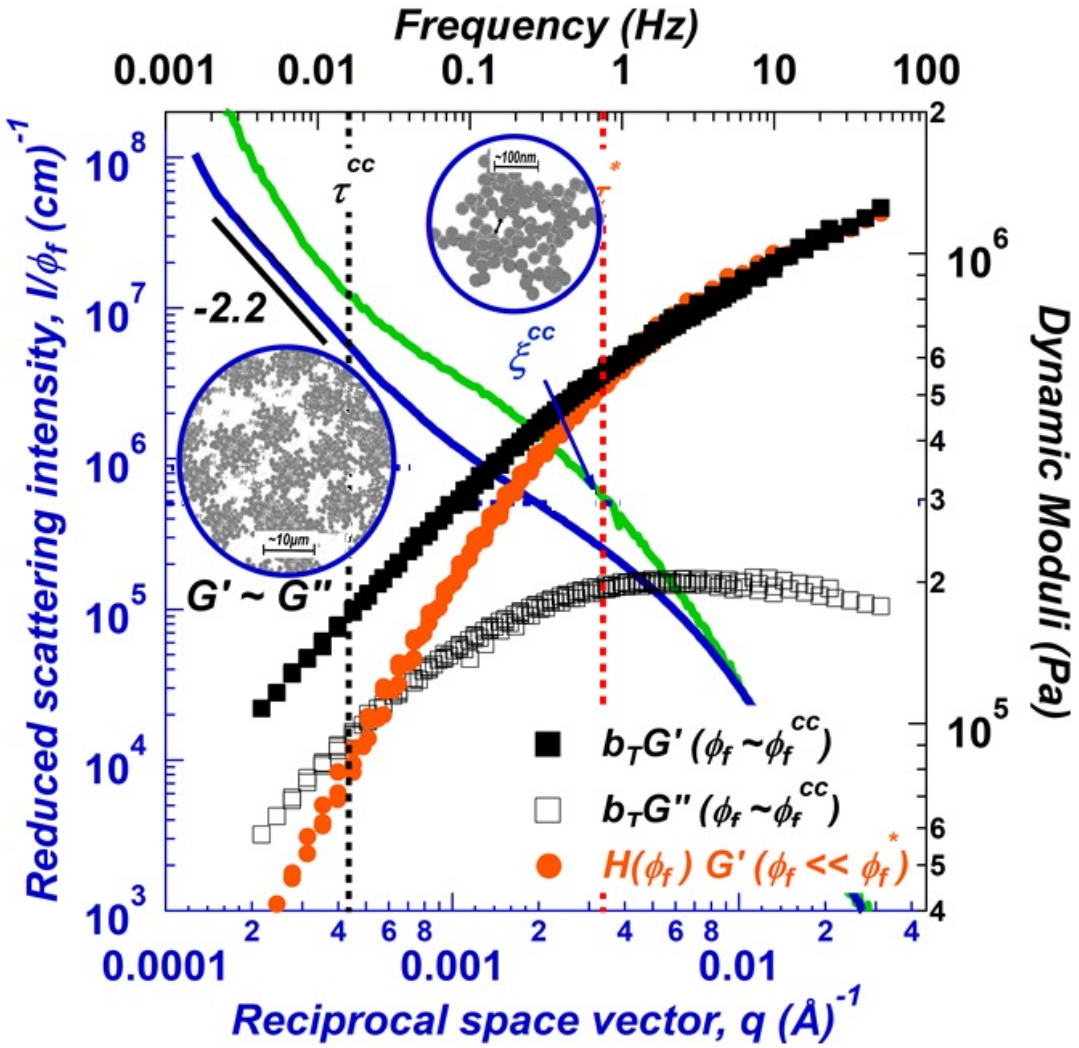
Rishi, K.; Pallerla, L.; Beaucage, G.; Tang, A. Dispersion of Surface-Modified, Aggregated, Fumed Silica in Polymer Nanocomposites. J. Appl. Phys. 2020, 127 (17), 174702.

Morphology from rheology

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

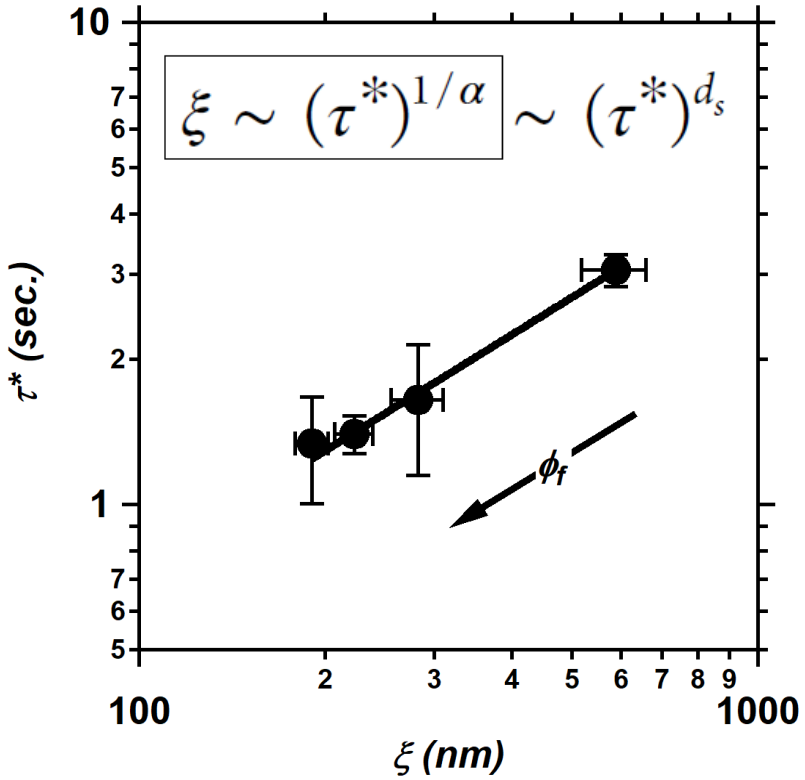


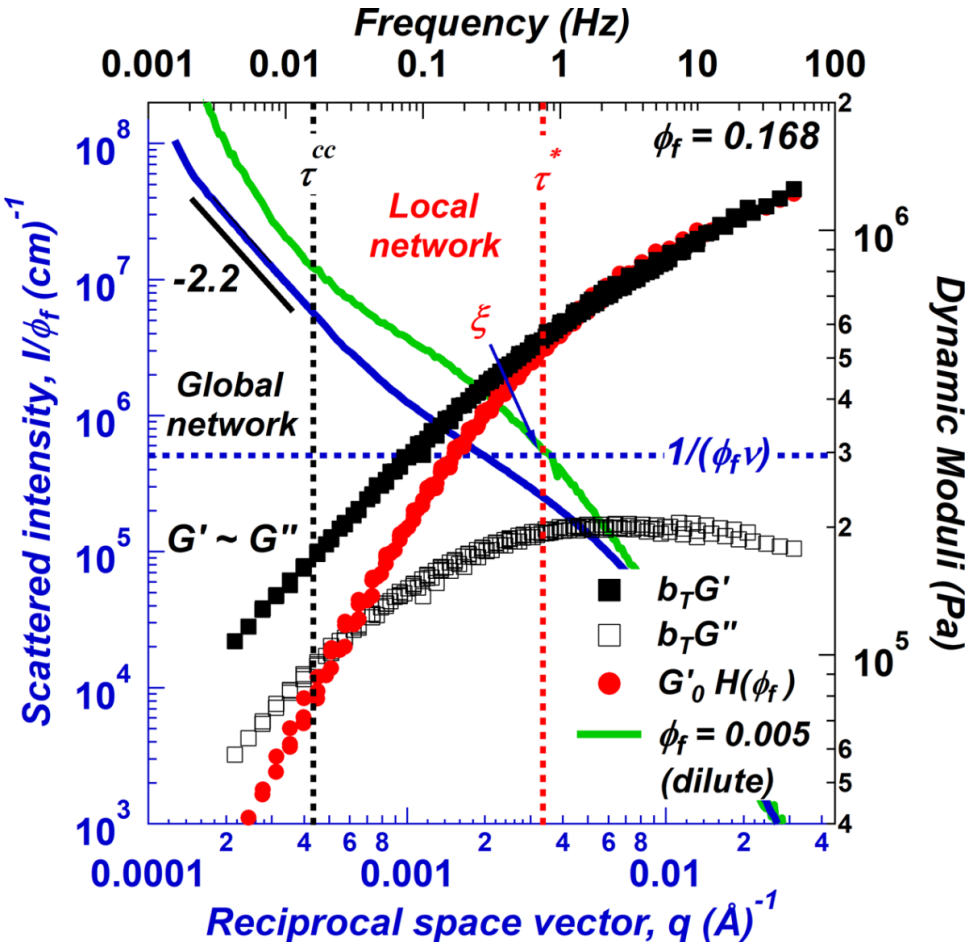
Filippone, G., Romeo, G. and Acierno, D., 2010. Viscoelasticity and structure of polystyrene/fumed silica nanocomposites: filler network and hydrodynamic contributions. *Langmuir*, *26*(4), pp.2714-2720.
Filippone, G. and Salzano de Luna, M., 2012. A unifying approach for the linear viscoelasticity of polymer nanocomposites. *Macromolecules*, *45*(21), pp.8853-8860.



- 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*

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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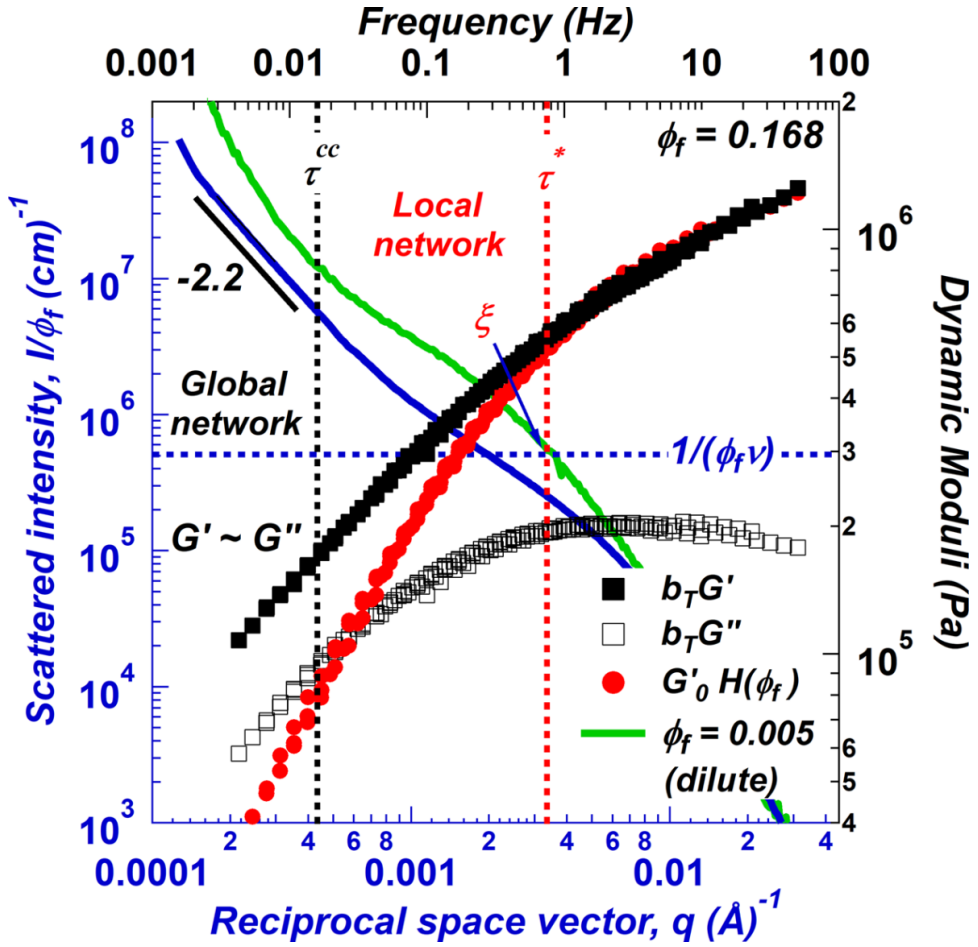
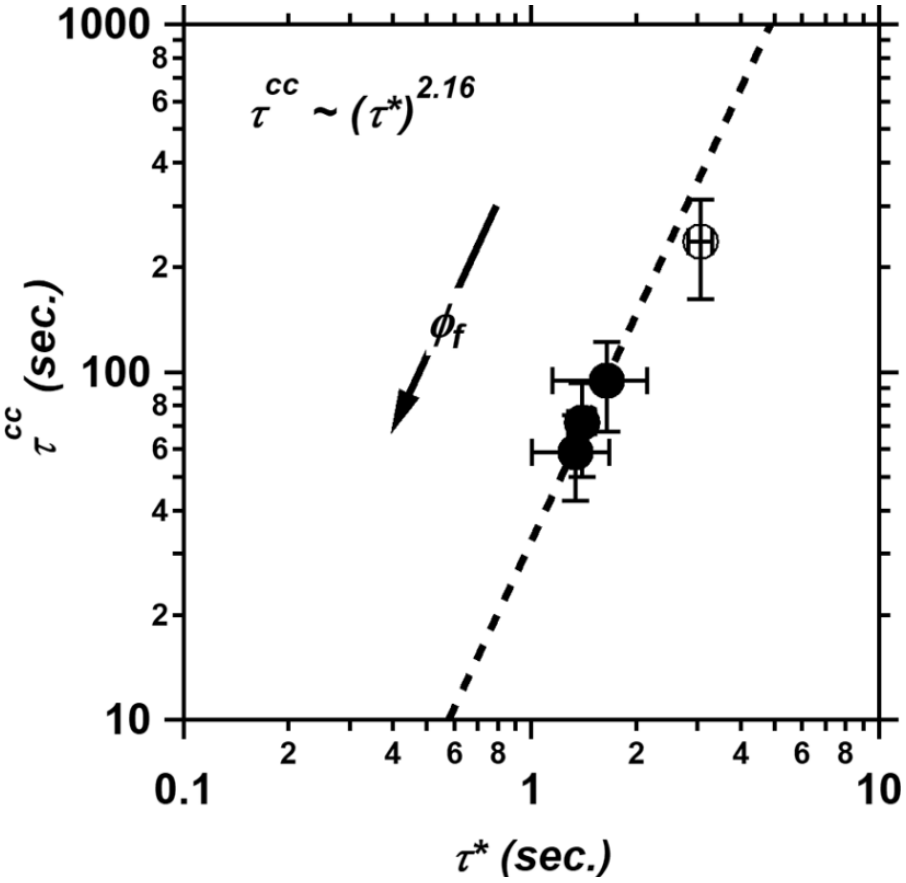
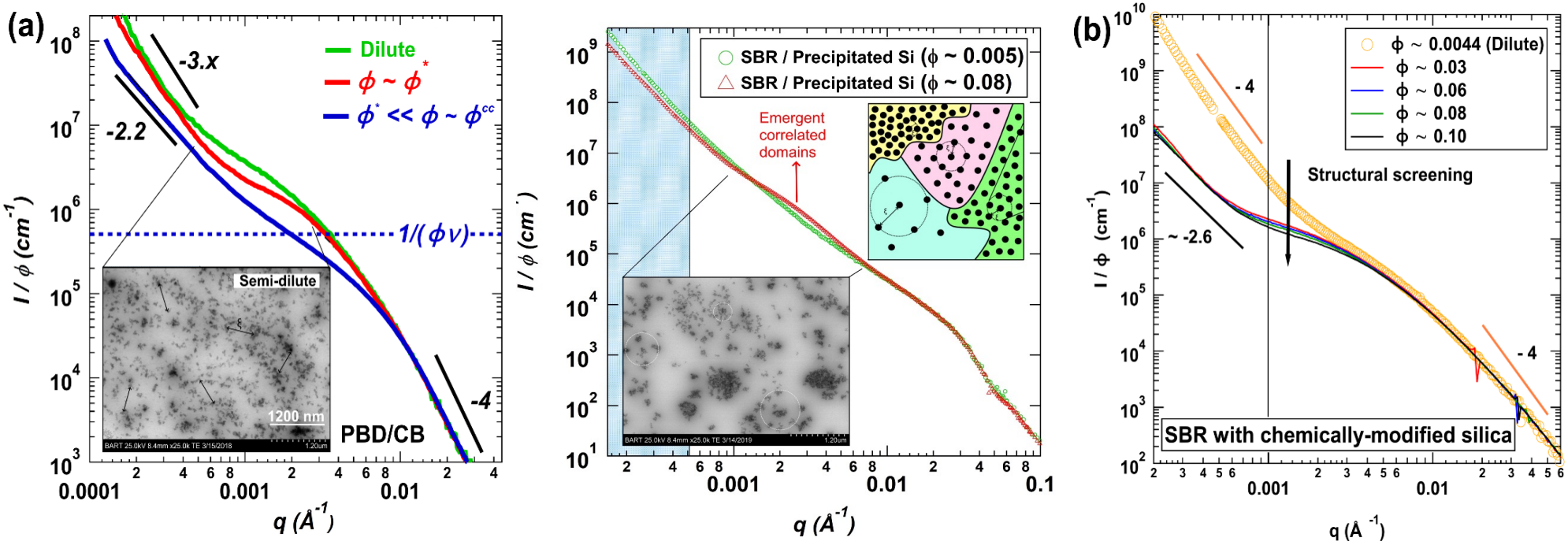




Rishi, K., Beaucage, G., Kuppa, V., Mulderig, A., Narayanan, V., McGlasson, A., Rackaitis, M. and Ilavsky, J., 2018. Impact of an emergent hierarchical filler network on nanocomposite dynamics. *Macromolecules*, *51*(20), pp.7893-7904.

Clustered aggregates to bulk network



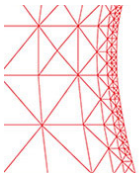
McGlasson, A., Rishi, K., Beaucage, G., Chauby, M., Kuppa, V., Ilavsky, J. and Rackaitis, M., 2020. Quantification of dispersion for weakly and strongly correlated nanofillers in polymer nanocomposites. *Macromolecules*, *53*(6), pp.2235-2248.

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.

Hierarchical emergent structure in commercial colloidal and polymeric systems

Greg Beaucage, Professor of Chemical and Materials Engineering
Kabir Rishi, PhD Candidate
Department of Materials Science & Engineering, University of Cincinnati

- There are multiple levels and not 1 that assemble from small to large sizes
- Primary particles decide aggregate structure, processing dictates changes to the aggregate structure and size
- Clustering of aggregates into local networks is dictated by the surface chemistry and kinetics.
- The formation of bulk network on the cm scale is dictated by the nature of clustered aggregates and the surface chemistry
- This constitutes a multiscale physics approach
- The point of compatibilization is to control immiscibility not to produce miscibility
- Link structure to dynamics in this complex system

Acknowledgements