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Project 5: Network/Reinforcing Filler Mechanical Response

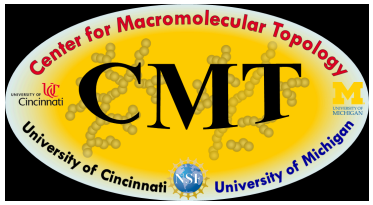
PI's: Greg Beaucage[1], Peter Green[2]

Team: Jan Ilavsky[3]

1 Univ. Cincinnati; 2 Univ. Michigan; 3 Argonne National Laboratory

Proposed Budget: $100,000/year; In Kind Support Argonne National Laboratory $40,000/year

Project Duration: 3 years



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Outcomes/Deliverables

- Demonstration of feasibility of the scaling approach to predict mechanical and dynamic mechanical properties of reinforces elastomers and isolated aggregates.
- Coupling of the scaling approach to Tom Witten theory for the mechanical properties of reinforced elastomers.
- Tune the dynamic mechanical response of reinforced elastomers using this approach.

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Impact

- Understanding the structure/property relationships of aggregate materials based on a topological description of the structure could pave the way for the design of improved reinforced elastomers.
- Understanding of structure/property relationships in reinforced elastomers.

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Prior work and project scope

- Scaling model for filler aggregates (G. Beaucage PRE 70 031401 (2004), D. Rai, G. Beaucage et al. submitted J. Phys. Chem. (2011).)
- Prior studies of reinforced elastomers by Beaucage and Green
- Prior work with DMA on nanocomposites by Green
- Witten predictions of mechanical properties for reinforced elastomers using scaling parameters (T. A. Witten, M. Rubinstein and R. H. Colby, Journal De Physique Ii **3** (3), 367-383 (1993). G. Huber, T.A. Vilgis, Kautschuk Gummi Kunststoffe 52 102-107 (1999). M. Klüppel, Adv. Polym. Sci. 164 1-86 (2003).)

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Prior work and project scope

Reinforcing fillers present a complex ramified morphology that has been characterized using various morphological models, chiefly those based on fractal scaling.

Prediction of properties from these models has not been successful because simple mass-fractal scaling cannot quantify topological features such as branching so is limited in predictive ability.

We have recently developed a method to quantify branching using scattering measurements that can be coupled with theories by Tom Witten to predict the static and dynamic mechanical response of isolated aggregates as well as reinforced elastomers.

This project couples quantification of aggregate topology with prediction of mechanical and dynamic mechanical behavior and measurement of dynamic properties using facilities at Argonne National Laboratory (APS), Cincinnati and Michigan.

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Supplementary Material

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Outline

Aggregate structure/property relationships

Structure of Filler Particles

Size Issues

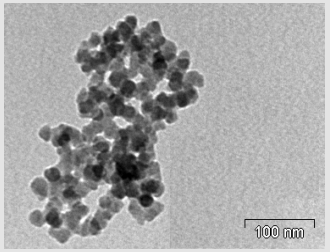
Why Fractal?

Fractal Properties

Statics

Dynamics

Small Angle Scattering



Structure-Property Relationships

Statics

Dynamics

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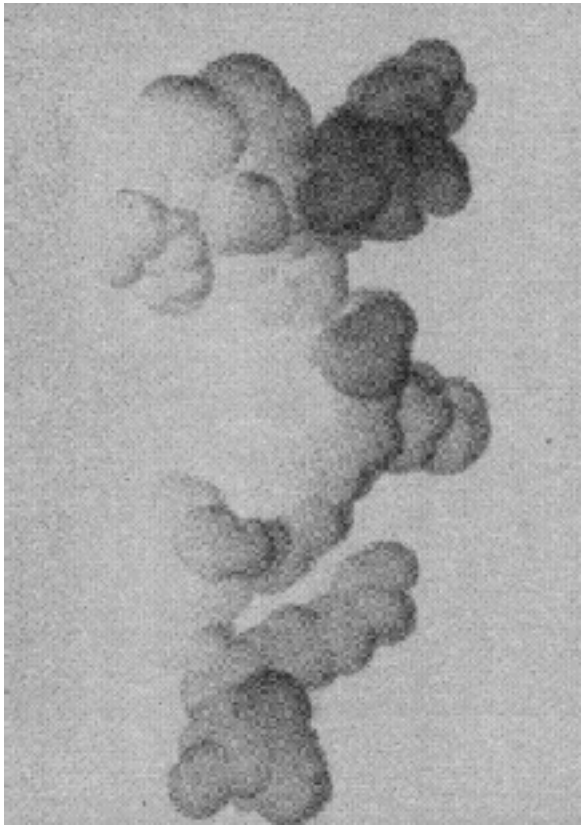
The Technological Approach: Serendipity

-Disordered materials
-Simple interfacial chemistry
-Tuned structure in existing reinforced elastomers begins on the nano-scale and is limited to sub-10 micron scales for homogeneity.
-Dynamic response is 2 orders and thermal is 200 °C range
-Dynamic strain amplitude is up to 10% in shear, tensile and compression
-Design has focused on reinforcing filler structure, simple chemical modification of filler interaction, polymer chemistry (block copolymers), additives



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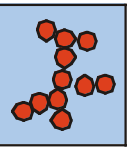
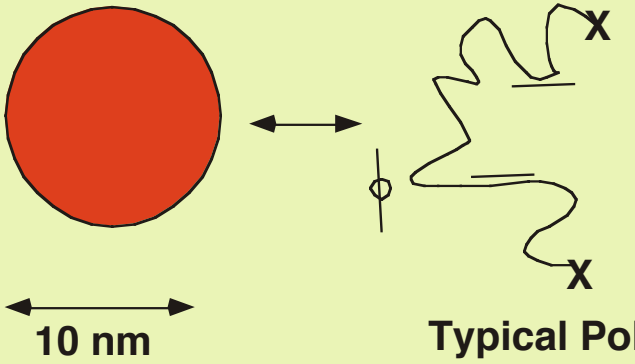
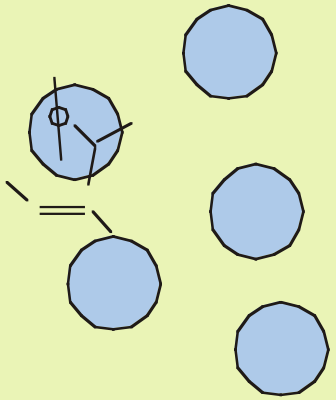
Polymer Networks/Elastomers/Filled Systems

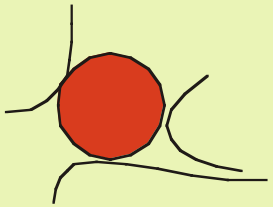
Consider Size Scales Polymer/Network vs Filler



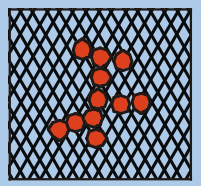
NANO-SCALE

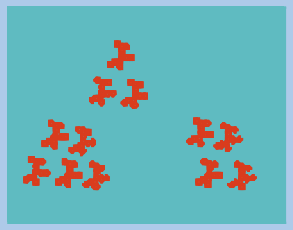






COLLOIDAL-SCALE





Empirical Choice of Filler Has Lead to Materials Near the Transition Between

1) Matrix is a Continuum to Filler (Aggregate) Rouse-Like Addition
2) Matrix is Comparable in Size to Filler (Primary) Complex Interplay Internal Filler Relaxations Important

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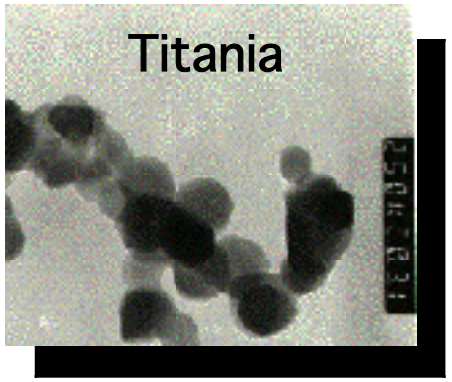
What is the Importance of Mass-Fractal Structure?

-Physically maintains surface area of particles

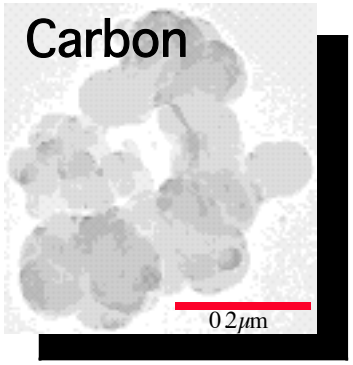
-Volume/mass ratio is high (occluded rubber)

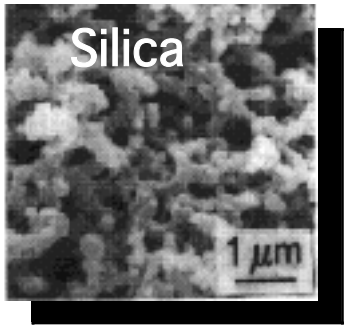
-Strong/stable structure
(or reversible aggregation)



-Dynamic response of filler particle adds athermally to the entropic elasticity of the rubber

-Aggregates can interlock/interact to form filler network





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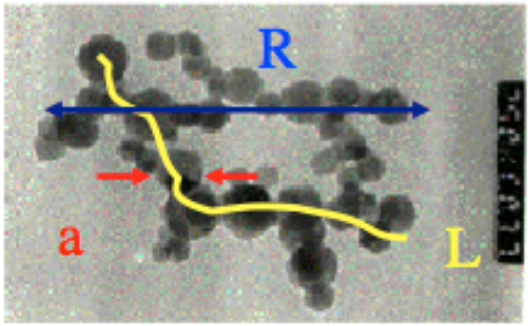
Mechanics Depend on Structure
Structure on Growth Chemistry



Mean Primary Particle Size, "a"

Mean Aggregate Size, "R"

Specific Surface Area related to 1/a

"R" is related to "a", "N", and Structure

"Structure" is Related to Growth Mechanism
"a" is Related to Early Stage
"N" and "R" to Later Stage

$N = a\,(R/a)^{d_f}$ How Dense?

$1 \le d_f \le 3$

$(L/a) = (R/a)^{d_{min}}$ Minimum Path Dim.

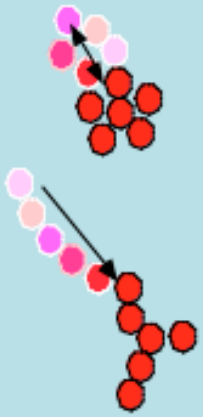
$1 \le d_{min} \le d_f$

$C = d_f/d_{min}$ How Branched?

Linear C = 1; Reg. C = d_f

Particle/Cluster, Denser

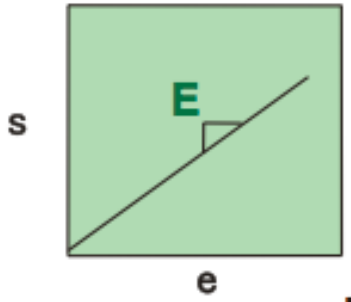
Cluster/Cluster, Looser



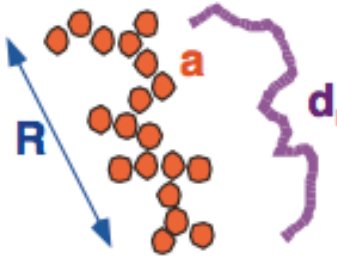
If Particles
Don't Stick Well
Packing is Dense
"Reaction Limited"

If Particles
Stick Immediately
Packing is Loose
"Diffusion Limited"

Nano-Aggregates Can Act as Springs



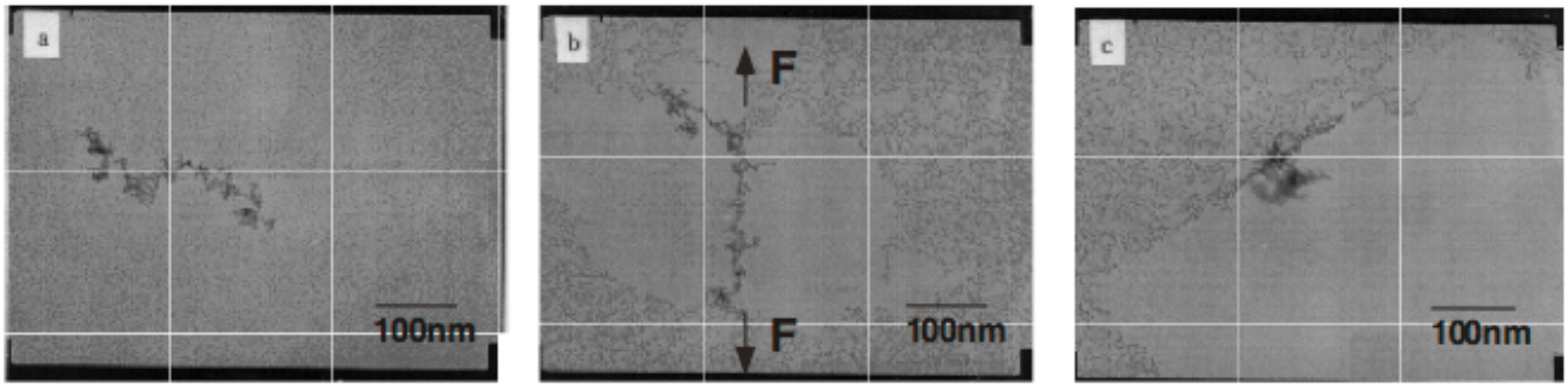
$$E_{Aggregate} = E_{Oxide}(a/R)^{3+d_{min}}$$



d_{min} is Dimension of Stressed Path

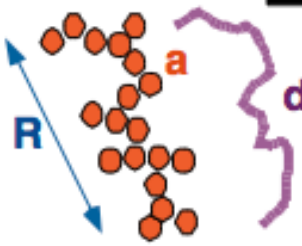
From: *T. A. Witten, M. Rubinstein, R. H. Colby*
J. Phys. II France 3, 367 (1993).

Static | Stressed | Released



From: *S. K. Friedlander, H. D. Jang, K. H. Ryu*
Appl. Phys. Lett. 72 173 (1998).

Summary of Witten/Rubinstein/Colby Theory for Mechanics of Springy Aggregates in Elastomers



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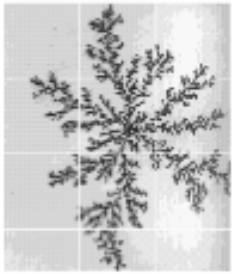


Aggregates are only Effective below a Critical Size, $R_{critical}$

$$R_{critical} = a(E_{Oxide}/E_{Rubber})^{1/(3+d_{min})}$$

A Critical Concentration is Predicted Beyond which There is No Higher Reinforcing Effect, $f_{critical}$

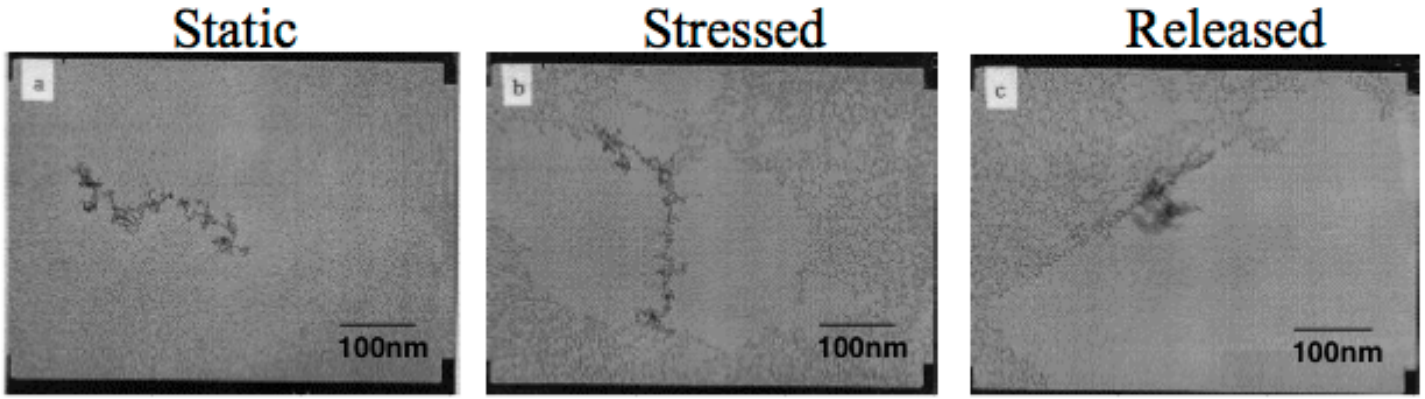
$$f_{critical} = (R/a)^{d_f-3}$$

The Modulus for a Critical Concentration Composite, $E_{composite}$ is given by:

$$E_{composite} = E_{Oxide}\, f_{critical}^{(3+d_{min})/(3-d_f)}$$

Test these Propositions using Tuned Nano-Composites

AGGREGATE BEHAVIOR AND TENSILE MODEL

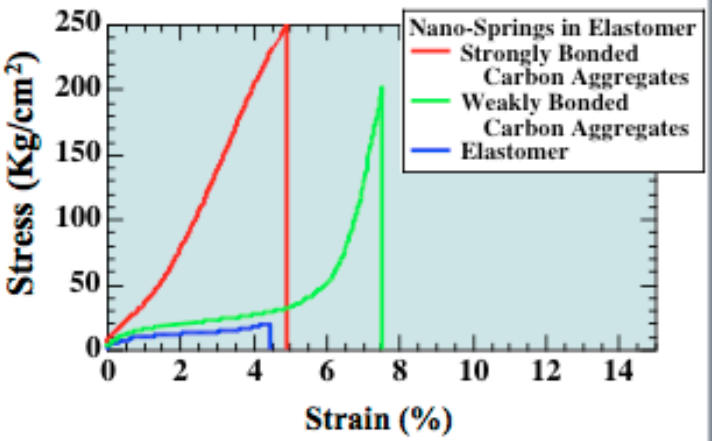


From: ***S. K. Friedlander, H. D. Jang, K. H. Ryu Appl. Phys. Lett. 72 173 (1998).***

$$\sigma = E^{*}\lambda^{P}$$

High Tensile Extension	
Weak Associations	Strong Associations
$P = 2(d_f - 1)/(d_{min} - d_f + 2)$	$P = (d_{min} + 1)/(d_{min} - 1)$

After: *T. Witten, et al, J. Phys. II France, 3, 367 (1993)*



After: *G. Kraus; Adv. Polym. Sci. 8, 155 (1971)*

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AGGREGATE VIBRATIONAL DYNAMICS

TABLE 1: Comparison of the Time Scales of Stretching and Contraction of Titania NCA

		Ogawa et al.[2]	present study
recording speed of camera (frames/s)		30	9000
primary particle diameter, d_0 (nm)		5.9	8.3
length of NCA (nm)		100	430
% deformation	stretching	74	10
	contraction	−68[a]	−22
time scale	stretching	~2 min	~1.6 ms
	contraction	<1/30 s	~1.3 s

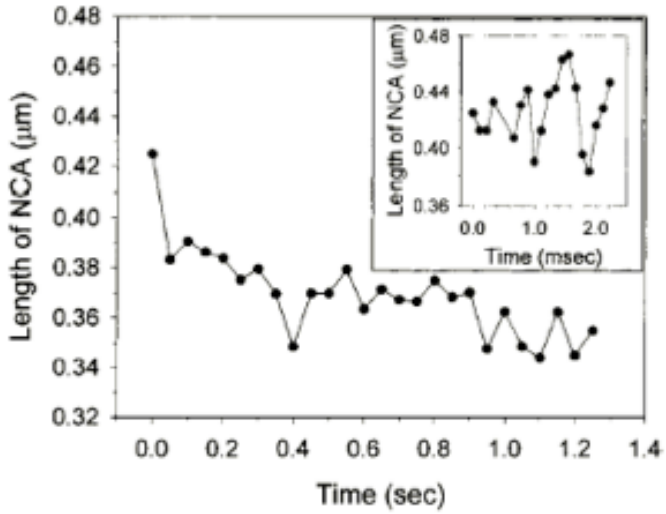
[a] For an NCA different from the one which stretched.

Relaxation time $\tau = \xi/\kappa$
In polymer ξ is
many orders higher
Harmonic oscillation is
probably on the order of
1 Hz in polymer

J. Phys. Chem. B, Vol. 105, No. 47, 2001 **11799**

In Vacuum:
Harmonic oscillation
with time constant on
the order of 0.5 msec

Exponential decay on the
order 0.2 second



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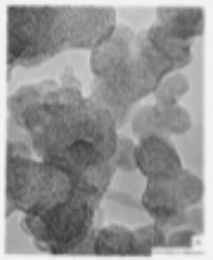
FILLER CHARACTERIZATION

Microscopy

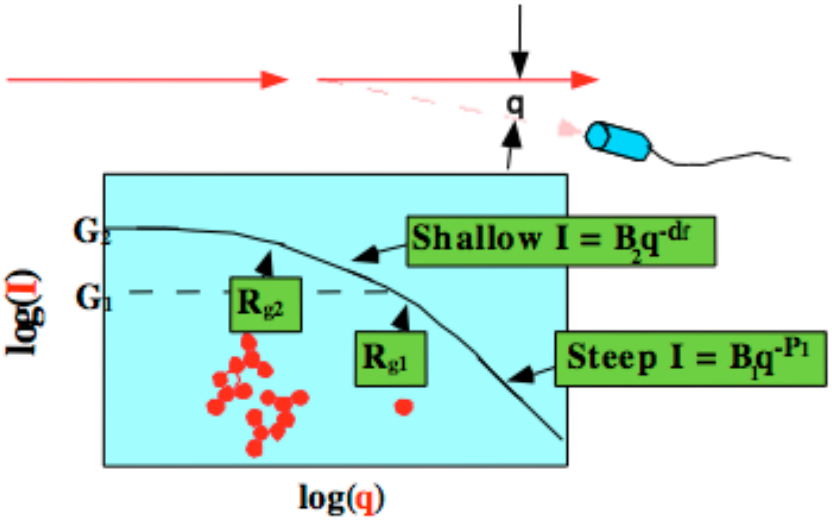


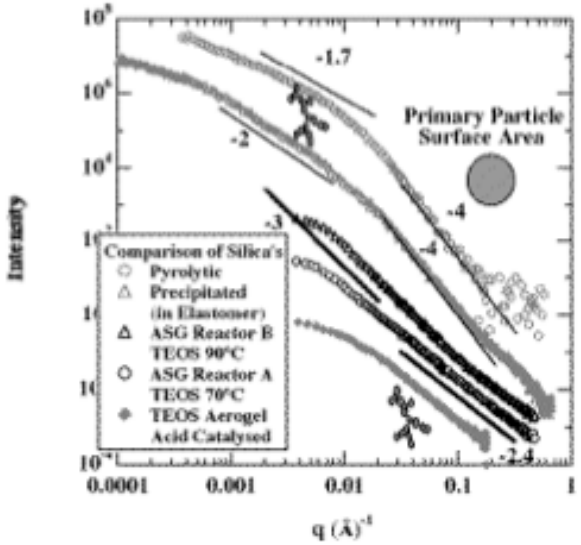
SEM
TEM

Surface Area/Structure

N_2SA, BET
CTAB
DBP

Small Angle Scattering





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MEASURED FEATURES => MECHANICAL RESPONSE

Fit Parameters: G_2, R_{g2}, B_2, d_f, G_1, R_{g1}, B_1

$$d_{\min} = \frac{d_f}{c} = \frac{B_2 R_{g2}^{d_f}}{G_2 \Gamma\left(d_f/2\right)}$$

$$\phi_{Br} = \frac{N-p}{N} = 1 - \left(\frac{R_{g2}}{R_{g1}}\right)^{d_{\min}-d_f}$$

$$n_{Br} = \phi_{Br} \frac{N}{\langle N_{Br} \rangle}$$

$E_{Aggregate}$
$E_{Composite}$

Aggregate Dynamic Response

Composite Dynamic Response

T. Witten, et al, J. Phys. II France, 3, 367 (1993)
Orbach, Nakayama, Yakubo Rev. Mod. Phys. 66(2) 381 (1994)
A. Izuka, H. H. Winter, T. Hashimoto, Macro. 30 6158 (1997)

Beaucage, *Phy. Rev. E*, **72** (2004)

Frequency Dependence of Mechanical Response at 30°C is Dominated by Filler and Filler Network

Orbach, Nakayama, Yakubo Rev. Mod. Phys. 66(2) 381 1994

$D(w) \sim w^{d-1}$ where d is the spectral dimension

D(w) is the density of states (mech. energy distribution)

(Alexander-Orbach and Rammal-Toulouse)

$d = 2d_f/d_w$ and $d \leq d_f \leq d$ (d and d_w are related to c and d_{min} measured by SAXS)

A. Izuka, H. H. Winter, T. Hashimoto, Macro. 30 6158 (1997)

$G'(\omega) = G''(\omega)/\tan\delta_c = S\,\omega^n\,\Gamma(1-n)\cos\delta_c$

For gels at percolation

We expect the filler network will show $G'' \sim G' \sim \omega^{d-1}$ and for some conditions $G'' \sim G' \sim \omega^{1/3}$ (Percolation)

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-Dynamic TEM (Friedlander) measurements indicate about 1Hz internal aggregate oscillation frequency for fractal aggregates

-We consider that the low-frequency response of reinforced elastomers is related to the internal filler structure, i.e. massfractaldimension,whilehigherfrequencyisrelated to the filler network within the polymer.

-We consider thermal/athermal elasticity in reinforced elastomers.

-Control will depend on time constant so stiffness of aggregate (want stiffer) and friction factor (smaller particles)

$$\tau \approx \xi/\varkappa$$

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Proposed Work

-Filler Structure property relationships using SAXS/TEM/DMA on industrial or model rubber compounds and model carbon and silica fillers

-Extension of correlation between dynamic properties and dimensional analysis of carbon and silica fillers

-In situ AFM/TEM stretching of aggregates and observation of the dynamic response