Computer Simulation for the Rheology of Worm-Like Micelle (WLM) Solutions

MD and Coarse Grain (DPD) Simulations- P&G Becket Ridge (Peter Koenig/Bruce Murch)

Diffusive wave spectroscopy (DWS)- P&G Mason, Ohio (Mike Weaver)

Traditional Dynamic Rheology- University of Michigan (Ron Larson)

Modeling of Rheology- University of Michigan (Ron Larson)

SANS- University of Cincinnati (Greg Beaucage/Karsten Vogtt)

Rheo-SANS- Oak Ridge National Laboratory, (Greg Smith/Jason Rich)

Other collaborations at P&G Cincinnati and Newcastle, Jeremie Gummel

Overview: Micelle Rheology Modeling Program



How do we know our models are correct?

Validating models using multiple techniques for internal consistency







Small-Angle X-ray and Neutron Scattering

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Small-angle scattering is used for:

- disordered materials networks, gels, ceramic aggregates (fumed silica and titania) and polymers;
- "d-spacings" and degree of order colloids, liquid crystals, block copolymers, and polymer lamellar crystallites;

3) orientation

BCP domains, polymer crystallites, rheosans;

4) detailed measures of structure viruses, proteins.

Small-Angle X-ray Scattering, (SAXS)

We Get Intensity as A Function of Angle

-Collimated Beam -Monochromatic Beam -Coherent Beam (-Focusing Optics Perhaps) -Longer Distance for Lower Angle

- -Large Dynamic Range Detector
- -Evacuated Flight Path

-Extend Angle Range with Multiple SDD's



Crystalline Reflections Can Also Be Used



X-ray versus Neutrons Scattering



X-rays interact with electrons Contrast is proportional to $(Dr_e)^2$ Electron density is a monotonic in atomic number

SAXS and XRD



Neutrons interact with atomic nucleii Contrast is proportional to (DS)² Neutron cross section S is random in the periodic table and changes With isotopes Biggest difference is between d and H

SANS and NPD

Neutron scattering has advantages for hydrogels, single chain scattering, Biomolecules such as proteins where D₂O can substitute for water.

However, neutron flux is much lower and SANS requires larger samples (1 cm diameter) and exposure time ~1 hour.

The Scattering Event



We can "Build" a Scattering Pattern from Structural Components using Some Simple Scattering Laws



First we will look at scattering from a single isolated particle, *Form Factor*.

Scattering from Dilute, Perfect, Monodisperse Objects Yields Interference Between Internal Structures (Form Factor)



Polydispersity & Asymmetry Lead to Smearing



We can use the <u>unified function</u> for polydisperse or asymmetric/oddly shaped, randomly-arranged structures.



1) Particle size distributions from small-angle scattering using global scattering functions. Beaucage G, Kammler HK, Pratsinis SE, J. Appl. Cryst. **37**, 523-535 (2004).

2) Structure of flame-made silica nanoparticles by ultra-small-angle X-ray scattering. Kammler HK. Beaucage G. Mueller R. and Pratsinis SE. Langmuir 20. 1915-1921 (2004).

3) Determination of branch fraction and minimum dimension of mass-fractal aggregates. Beaucage G. Phys. Rev. E. 70, 031401 (2004).

4) Approximations leading to a unified exponential/power-law approach to small-angle scattering. Beaucage G. J. Appl. Crystallogr. 28. 717-728 (1995).

5) Small-Angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension. Beaucage G. J. Appl. Crystallogr. 29. 134-146 (1996).

Correlation Leads to a Characteristic Change in the Shape of the Scattering Curve (Structure Factor)



x is the correlation distance (an average d-spacing) k is the packing factor, $k = 8 V_{hard core}/V_{available}$ (0 to 5.92)

Correlation Leads to a Characteristic Change in the Shape of the Scattering Curve (500 Ang. Spheres)



x is the correlation distance (an average d-spacing) k is the packing factor, $k = 8 V_{hard core}/V_{available}$ (0 to 5.92) Correlation Leads to a Characteristic Change in the Shape of the Scattering Curve



x is the correlation distance (an average d-spacing) k is the packing factor, $k = 8 V_{hard core}/V_{available}$ (0 to 5.92)

Correlation Leads to a Characteristic Change in the Shape of the Scattering Curve



Linear Plot may be better for correlations.



¹⁾ Multiple Size-Scale Structures in Silica-Siloxane Composites Studied by Small-angle Scattering. Beaucage G. Ulibarri TA. Black EP. Schaefer DW. ACS Symposium Series 585, 97-111 (1995). See my web page for a scan of this reference.

Construction of A Scattering Curve For a Mass Fractal Aggregate with no Correlations



Guinier's Law





1) Particle size distributions from small-angle scattering using global scattering functions. Beaucage G, Kammler HK, Pratsinis SE, J. Appl. Cryst. 37, 523-535 (2004).

2) Structure of flame-made silica nanoparticles by ultra-small-angle X-ray scattering. Kammler HK, Beaucage G, Mueller R, and Pratsinis SE, Langmuir 20, 1915-1921 (2004).



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<u>3) Determination of branch fraction and minimum dimension of mass-fractal aggregates. Beaucage G. Phys. Rev. E, 70, 031401 (2004).</u>
<u>4) Approximations leading to a unified exponential/power-law approach to small-angle scattering. Beaucage G. J. Appl. Crystallogr. 28, 717-728 (1995).</u>
<u>5) Small-Angle Scattering from Polymeric Mass Fractals of Arbitrary Mass-Fractal Dimension. Beaucage G. J. Appl. Crystallogr. 29, 134-146 (1996).</u>





 $I(q) = B_P q^{-4}$









dimension of fractal aggregates Phys. Rev. E 70 031401 (2004).²⁸





-Behavior is Similar to Simulation d_f drops due to branching

-Aggregate Collapse

-Entrainment High in the Flame

Particle Size, d_p





Figure 1. An USAXS pattern of agglomerated fumed silica (Aerosil 200, Degussa AG). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, three Porod regimes (dashed line, dashed-dotted line, and long-short-dashed line) are shown together with the Guinier regimes (dotted line and dashed-double-dotted line). The appearance of the second Porod (weak power-law) regime (0.0005 Å⁻¹ < q < 0.01Å⁻¹) proves that these particles are agglomerated and mass fractal as shown by the TEM insert. The gray shaded area indicates the integral part for determining the second se nation of dys.



Figure 2. A USAXS plot of a nonagglomerated fumed silica (Si-B 32) made in a 17 g/h sustained premixed flame reactor (ref 18). The scattering data (circles) are well described by the global unified fit equation (solid line). Furthermore, Porod regimes (dashed line and long-short-dashed line) are shown together with the Guinier regime (dotted line). The lack of the Porod (weak power-law) regime at 0.0005 Å⁻¹ < q < 0.005 Å⁻¹ indicates that the particles are nonagglomerated as shown by the TEM insert. The gray shaded area indicates the integral part for determination of d_{WS} .



Figure 3. Comparison of d_{WS} and d_{BET} for agglomerated silica powders made in our vapor- or liquid-fed flame aerosol reactors (refs 18 and 20–22) and those of commercially available powders (Aerosil 200 and Aerosil 380, Degussa AG).



Figure 4. Comparison of d_{WS} and d_{BET} for various nonagglomerated silica powders made in our vapor-fed (refs 18 and 19) and liquid-fed (ref 20) flame aerosol reactors.

Structure of flame made silica nanoparticles by ultra-snallangle x-ray scattering. Kammler HK, Beaucage G, Mueller R, Pratsinis SE Langmuir 20 1915-1921 (2004).

Particle Size Distribution Curves from SAXS

PDI/Maximum Entropy/TEM Counting



Figure 2

USAXS data from aggregated nanoparticles (circles) showing unified fits (bold grey lines), primary particle Guinier and Porod functions at high q, the intermediate mass fractal scaling regime and the aggregate Guinier regime (dashed lines). (a) Funed titania sample with multi-grain particles and low-q excess scattering due to soft agglomerates. $d_{VIS} = 16.7 \text{ nm}$ (corrected to 18.0 nm), PDI = 3.01 ($\sigma_g = 1.35$), $R_g = 11.2 \text{ nm}$, $d_e = 1.99$, $z_{21} = 175$, $z_{R_g} = 226$, $R_{g2} = 171 \text{ nm}$. From gas adsorption, $d_p = 16.2 \text{ nm}$. (b) Funed zirconia sample (Mueller *et al.*, 2004) with single-grain particles, as shown in the inset. The primary particles for this sample have high polydispersity leading to the observed hump near the primary particle scattering regime. $d_{VIS} = 20.3 \text{ nm}$, PDI = 10.8 ($\sigma_g = 1.56$), $R_g = 26.5 \text{ nm}$, $d_g = 2.90$. From gas adsorption, $d_p = 19.7 \text{ nm}$.

Particle size distributions from small-angle scattering using global scattering functions, Beaucage, Kammler, Pratsinis J. Appl. Cryst. <u>37</u> 523-535 (2004).



Figure 6

Comparison of particle volume distributions for titania made without an electric field using TEM (circles; Kammler *et al.*, 2003), PDI (grey line) and maximum entropy (black line). (a) 0.5 gh⁻¹ [fractal $d_{VIS} = 12.1$ nm, PDI = 3.52 ($\sigma_g = 1.38$), $R_g = 8.9$ nm, $d_g = 1.59$, $z_{24} = 1160$, $z_{R_g} = 1343$]. (b) 55 g h⁻¹ [$d_{VIS} = 37.2$ nm, PDI = 20.0 ($\sigma_g = 1.65$), $R_g = 50.8$ nm]. (c) 11 g h⁻¹ [$d_{VIS} = 46.8$ nm, PDI = 155 ($\sigma_g = 1.61$), $R_g = 60.8$ nm]. (3 g h⁻¹ is shown in Fig. 5.)

Compatibility/Miscibility/Shelf Life for Colloidal Mixtures

Butadiene/Carbon Black Samples March 2015

	Carbon Black Weight Percent			
Polymer	1	5.6	15.1	29.9
BR1	BR1-1	BR1-5	BR1-15	BR1-30
BR2	BR2-1	BR2-5	BR2-15	BR2-30
BR3	BR3-1	BR3-5	BR3-15	BR3-30

Table 1. Samples studied.

$$I_{0}(q) = \sum_{1}^{3} \left\{ G_{i} e^{\left(-q^{2} R_{i}^{2} / 3\right)} + e^{\left(-q^{2} R_{i}^{2} / 3\right)} B_{i} q^{*-P_{i}} \right\}$$
(2)

where level 1 pertains to a graphitic layer, level 2 to the primary particles and level 3 the aggregate structure.



Figure 3. Plot of the three one percent carbon black reinforced polymers and the carbon black powder. A four level unified fit to the BR1-1 samples is shown. Values of $1/(v\phi_m)$ are also plotted for comparison with the scattering curve.



Figure 4. Scattered intensity divided by the mass concentration for various concentrations of carbon black in BR1. Intensity at intermediate-q drops with concentration following equation 3. Values of $1/(v\phi_{wt})$ are also plotted for comparison with the scattering curves $v = 3.08 \times 10^{-6}$ cm.

Osmotic Approach to Reinforcing Filler Compatibility

$$\frac{\pi}{kT} = \phi_{\text{num}} + B_2 \phi_{\text{num}}^2 + B_3 \phi_{\text{num}}^3 + \dots$$
(1)

where ϕ is the number density of particles or molecules. B₂ reflects the enhancement of osmotic pressure due to binary interactions of a colloid in a matrix in terms of the thermal energy, kT. B₂ is related to an integral of the interaction energy between particles. Such a binary interaction



Osmotic Pressure

Solute molecules move with kT and exert a pressure like a gas on the walls of the vessel. This is the osmotic pressure.

We can use this to count the number of solute molecules, n (π is a colligative property). For a known mass used to make the solution we can obtain the number average molecular weight.


A parallel definition of the second virial coefficient using the mass density concentration, ϕ_{mass} , rather than the number density concentration, ϕ_{num} , is possible,

$$\frac{\pi}{RT} = \frac{\phi_{mass}}{M} + A_2 \phi_{mass}^2 + A_3 \phi_{mass}^3 + \dots$$
(2)

where M is the molecular weight of a particle. $\phi_{mass} = M\phi_{num}/N_a$, where N_a is Avogadro's number, and $A_2 = B_2 N_a/M^2$, following Bonneté et al..[13] B_2 is related to the binary interaction potential for particles, U(r), by,

$$B_{2} = 2\pi \int_{0}^{\sigma} r^{2} \left(1 - e^{-U(r)/kT}\right) dr$$
(3).

 B_2 has units of ml/particle, and A_2 has units of mole ml/g². If a hard core potential is assumed, then the hard core radius, σ_{HC} , is given by,

$$\sigma_{HC} = \left(\frac{3A_2M^2}{2\pi N_a}\right)^{\frac{1}{3}} = \left(\frac{3B_2}{2\pi}\right)^{\frac{1}{3}}$$
(4).

 $\sigma_{\rm HC}$ should be a size scale on the order of the size of an aggregate so this serves as a check for the validity of the second virial coefficient.

DPD simulations and the Second Virial Coefficient

The second virial coefficient can be used to predict stability and compatibility of elastomer/filler systems. For this purpose DPD (dissipative particle dynamics) simulations are often used. A typical repulsive potential for a DPD system is of the form,[14]

$$\frac{U(r)}{kT} = \frac{A}{2} \left[1 - \left(\frac{r}{\sigma}\right) \right]^2 \tag{5}$$

where σ is the diameter of the aggregates, and A is a dimensionless binary short range repulsive amplitude that can be defined for the particle interactions that are at play in a specific situation.

$$\frac{\phi_w}{I(q)} = \frac{\phi_w}{I_0(q)} + \upsilon \phi_w$$

where v is related to the second virial coefficient by,[18, 21]

$$A_2 = \left(\frac{\nu \left< \Delta \rho^2 \right>}{N_a \rho^2}\right)$$

 $B_2 = M^2 A_2 / N_a = [z \rho_{carbon} (4\pi (d_p/2)^3/3)]^2 A_2 / N_a$



Polystyrene in d-Toluene

Scattering Functions of Semidilute Solutions of Polymers in a Good Solvent

JAN SKOV PEDERSEN,¹ PETER SCHURTENBERGER²

Journal of Polymer Science: Part B: Polymer Physics, Vol. 42, 3081-3094 (2004)

39

(3)

(4)

 $I_0(q) = \sum_{1}^{3} \left\{ G_i e^{\left(-q^2 R_{ss}^2/3\right)} + e^{\left(-q^2 R_{ss}^2/3\right)} B_i q^{*-P_i} \right\}$

$$\frac{\phi_w}{I(q)} = \frac{\phi_w}{I_0(q)} + \upsilon \phi_w$$



Organic pigment in aqueous suspensio n

(2),

(3)

40

$$\frac{\phi_{w}}{I(q)} = \frac{\phi_{w}}{I_{0}(q)} + \upsilon \phi_{w}$$

where v is related to the second virial coefficient by,[18, 21]



Figure 1. Schematic of the screening effect and scattering in the semi-dilute regime.

(3)



Figure 2. Schematics of formation of agglomerate superstructure in the concentrated regime from the third structure in Figure 1. Top fractal super structure. Bottom domain super structure.

 $I_0(q) = \sum_{1}^{3} \left\{ G_i e^{\left(-q^2 R_{ss}^2/3\right)} + e^{\left(-q^2 R_{ss}^2/3\right)} B_i q^{*-P_i} \right\}$

$$\frac{\phi_w}{I(q)} = \frac{\phi_w}{I_0(q)} + \upsilon \phi_w$$



Organic pigment in aqueous suspensio n

(2),

(3)

43



Figure 4. Scattered intensity divided by the mass concentration for various concentrations of carbon black in BR1. Intensity at intermediate-q drops with concentration following equation 3. Values of $1/(v\phi_{wt})$ are also plotted for comparison with the scattering $curve_{RA}v = 3.08 \times 10^{-6}$ cm.

	Gi,	Rei,	Bi, cm ⁻¹	Pı	G2,	R.2,	B2, cm ⁻	P2	Ga,	R _{g3} ,	Ba, cm ⁻	P3	B4, cm ⁻	P4
	cm-I	Å	Å-PI		cm ⁻¹	Å	I <mark>Å</mark> -₽2		cm ⁻¹	Å	I <mark>Å</mark> -₽3		I <mark>Å</mark> ₽I	
CB	6e-3	16.0	-2.5E-5	2	3.06	134	3.8E-7	4	1713	2633	8.3E-4	2.26	4E-6	3.02
BR1-1	10	15.6	0.104	2	6755	166	2.3E-4	4	7E6	2066	1.41	2.15	3.0E-3	2.58
BR2-1	10	14.9	0.851	2	8935	181	2.4E-4	4	6E6	2066	2.01	2.08	1.6E-4	3.06
BR3-1	10	11.5	0.101	2	9430	175	2.4E-4	4	8E6	2389	2.05	2.08	1.6E-4	3.04

Table 2. Fit Parameters for the 1 percent BRs and Carbon Black Powder Samples.

Table 3. Calculated parameters for the BR1 and carbon black powder samples from the third structural level.

	z	d	c	dr	C _p	р	Reed, nm	d _e , nm	PDI	۵¢	μ, nm
CB Powder	560			2.26							
BR1-1	1000	1.79	1.21	2.15	1.65	302	318	13.1	14.4	1.60	45.3
BR2-1	670	1.75	1.19	2.08	1.55	237	325	14.3	14.4	1.60	49.1
BR3-1	850	1.78	1.17	2.08	1.6	319	375	14.7	11.3	1.57	54.7
Mean	840						339	13.9			



Figure 5. Scattered intensity divided by the mass concentration for BR1-1 and BR1-30. Fits using equation 3 are shown. v is 3.08 x 10° cm for both fits. Values of $1/(v\phi_m)$ are also plotted for comparison with the scattering curve.

Table 4. Values of v and A₂ from equations 3 and 4. B₂ calculated from A₂, σ_{BC} from equation 1d, and "A" from equation 1f using $\sigma = \langle R_{eted} \rangle$ from Table 2.

	v, 10 ⁻⁶ cm	A , 10 mole ml/g	B., 10 ml/Aggregate	σBC, nm	DPD "A" $(\sigma = 339, nm)$
BR1	3.08 ± 0.8	0.998	3.20	248	17.5
BR2	3.26 ± 0.8	1.06	3.39	253	19.8
BR3	3.91 ± 1.4	1.27	4.06	269	31.3



Figure 7. Graphical comparison of v for each polymer/carbon black mixture.



Figure 8.Calculation from equation (3) for B_2 based on the average end to end distance from Table 4. Horizontal lines show the experimentally measured values for B_2 .

Summary

-Reinforced elastomer composites were examined using a new application of the second virial coefficient to describe compatibility of carbon black with three different butadiene elastomers.

-It was found that this approach distinguishes compatibility changes for the three elastomers.

Ultra small-angle x-ray scattering was used to measure the scattering pattern at several concentrations of carbon black. Changes in scattering with concentration were described with a single second virial coefficient for each elastomer using a scattering function related to the random phase approximation.

-The approach seems applicable to a wide range of nano composite materials. Values for the repulsive interaction potential parameter, "A" in the DPD method were estimated for the three samples. These values could be used in coarse grain computer simulations of filler segregation in these elastomers.

Chain and Gel Structure using SAXS/SANS





Persistence is distinct from chain scaling



Branching has a quantifiable signature.





Branching dimensions are obtained by combining local scattering laws

Chain persistence







PHB = polyhydroxybutyrate (side chain = -CH3) PHV = polyhydroxyvalerate (side chain = -CH2CH3)

These are short chain branching similar to branching in polyolefins

Persistence length of isotactic poly(hydroxyl butyrate) Beaucage G, Rane S, Sukumaran S, Satkowski MM, Schechtman LA, Doi Y *Macromolecules* **30 4158-4162 (1997).** *Rheology and persistenc in polyhydroxy alkonates.* Ramachrichnan R, Beaucage G, Satkowski M, Melik D in preparation *J. Rheology.*

Chain persistence



Persistence length of isotactic poly(hydroxyl butyrate) Beaucage G, Rane S, Sukumaran S, Satkowski MM, Schechtman LA, Doi Y *Macromolecules* **30 4158-4162** (1997). *Rheology and persistenc in polyhydroxy alkonates*. Ramachrichnan R, Beaucage G, Satkowski M, Melik D in preparation *J. Rheology*.



Intrinsic and Topological Stiffness in branched polymers. Connolly R, Bellesia G, Timoshenko EG, Kuznetsov YA, Elli S, Ganazzoli G Macromolecules 38 5288-5299 (2005).

Fractal Structure Overview -Mass Fractal Dimension -Other Dimensions -Calculation of Branching -Examples

1) Mass Fractal dimension, d_f.



$$z = \alpha \left(\frac{2R}{d_p}\right)^{d_f} \quad z \text{ is mass/DOA} \\ \begin{array}{c} \mathsf{d}_{\mathsf{p}} \text{ is bead size} \\ \mathsf{R} \text{ is coil size} \end{array}$$

Random aggregation (right) $d_f \sim 1.8$; Randomly Branched Gaussian $d_f \sim 2.5$; Self-Avoiding Walk $d_f = 5/3$

Problem:

Disk $d_f = 2$ Gaussian Walk $d_f=2$



Nano-titania from Spray Flame

 $2R/d_p = 10, a \sim 1, z \sim 220$ $d_f = ln(220)/ln(10) = 2.3$

A Measure of Branching is not Given.



2) Fractal dimensions (d_f, d_{min}, c) and degree of aggregation (z)



d_{min} should effect perturbations & dynamics.

Beaucage G, *Determination of branch fraction and minimum dimension of frac. agg.* Phys. Rev. E **70** 031401 (2004). Kulkarni, AS, Beaucage G, *Quant. of Branching in Disor. Mats.* J. Polym. Sci. Polym. Phys. **44** 1395-1405 (2006). 61



backbone particles

inelastic dead ends

2: cluster size

Fractal aggregates are springs



Initial Stage



Hole growth and stretching of the NCA





Maximum strotch achieved through hole growth

FIG. 7. Schematics of hole formation and stretching.



first changes in the NCA



NCA breaks loose at one end and snaps back



FIG. 9. Elastic behavior of titania NCA. (a) Initial shape of NCA on an ultrathin carbon film. (b) The NCA began to stretch as a hole developed in the carbon film after 7.5 min. (c) The NCA stretched by 36% after 10 min. (d) Contracted NCA after the anchor point to the film (bottom right) broke at 11.3 min.

Ogawa K, Vogt T., Ullmann M, Johnson S, Friedlander SK, Elastic properties of nanoparticulate chain aggregates of TiO₂, Al₂O₃ and Fe₂O₃ generated by laser ablation, J. Appl. Phys. 87, 63-73 (2000).

A Scaling Model for Branched Structures Including Polyolefins



$$\phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c - 1}$$

Mole Fraction of Branches

Beaucage G, *Determination of branch fraction and minimum dimension of fractal aggregates* Phys. Rev. E **70** 031401 (2004).



Branching dimensions are obtained by combining local scattering laws

Mole Fraction of Branches



p = 24 & z = 39 f_{Br} = (39-24)/39 = 38.5 Mole %

$$p = 1 \& z = 2$$

 $f_{Br} = (2-1)/2 = 50$ Mole %

$$p = 2 \& z = 6$$

 $f_{Br} = (6-2)/6 = 66.7$ Mole %



	F5	F2
$\overline{M_w(\mathrm{g/mol})}$	2×10^{6}	18×10^{6}
G(arb. units)	1376 ± 8	38 ± 1
$R_{g}(\text{\AA})$	$197\!\pm\!1$	$268\!\pm\!10$
B_f	$0.0448 \!\pm\! 0.0004$	0.00035
d_f	2.05	2.15
<i>d</i> _{min} ———	1.67	1.64
С	1.23	1.36
Ζ	19 200	173 000
$\phi_{ m br}$	0.84	0.94

4) Branched Polymers at Thermal Equilibrium: Model Systems for LCB



For Polymers d_{min} is the Thermodynamically Relevant Dimension (5/3 = 1.67 or 2)

 $d_f = d_{min} c$ ~ thermo x branching

Mole fraction of Branches



FIG. 1. 2D schematic sketches of aggregates with similar R_g . (a) Linear aggregate and (b) a branched fractal aggregate of identical p but different z and d_f , as described in the text.

$$\phi_{\rm br} = \frac{z-p}{z} = 1 - z^{1/c-1} = 1 - \left(\frac{R_{g,2}}{R_{g,1}}\right)^{d_{\rm min}-d_f}$$

4) Six Arm Polyurethane Star Polymers



PDI ~ 4 Arm M_w ~ 2,000 g/mole



Kulkarni A, Beaucage G using Data of Jeng, Lin et al *App. Phys. A* (2002)





PDI ~ 4-5

 $\phi_{\rm br}$

4) Hyperbranched Polymers Phase Separation at High MW Due to Branching





4) Hydrogenated Polybutadiene

Model hydrogenated/ deuterated Polybutadiene

-Used as a <u>linear standard</u>
for polyethylene
-There is a possibility of long
chain branching through
reaction of pendent
unsaturation during
butadiene polymerization
prior to hydrogenation

PDI = 1.02 M_w ~ 28,000 g/mole



q (Å)

Richter, Fetters et al. Macromol. Chem. Phys. (2000)

Gel Types: A Structural View

Polymer Gels

Chemical Networks Radiation crosslink Chemical Crosslink





Semi-crystalline

Gels



Block Co-polymer

Gels (hydro-phobic/

philic, glassy

domains,)





Layered silicate aqueous (clay) gels

Structural Gels Typically long gelation time

High shear sensitivity

Non-degradable but shear thinning



Semi-crystalline gels Relatively sharp thermally/or solvation induced gellation

SANS can study development/modification of gel structure. We have studied supercritically extracted gels with SAXS and Semi-crystalline Gels with SANS



Figure 1. Comparison of an integral calculation for a platelet and the unified function using the same three parameters. Oscillations in the parallelipid calculation at high-q are due to monodispersity in the thickness. Generally, sample thicknesses are sufficiently polydisperse to not display these oscillations.

Scattering from randomly arranged platelets displays two size scales, t and D and a power -2 scaling regime









Nano-Structured, Semicrystalline Polymer Foams. J. Polym. Sci., Part B: Polym. Phys. **34**(17), 3063-3072 (1996).
Gel scattering versus dense phase scattering.



Figure 2. Scattering data from polyacrylonitrile foam. SALS, USAXS, SAXS, and XRD data. SALS data has been scaled to match the intensity of the USAXS curve. Others are in absolute intensity. For the 3 parameter fit t = 86 Å and $R \approx 1953$. Portions of the combined data set were previously published.²³





Figure 3. Scattering data for conventional melt crystallized polymers, HDPE with fibrillar, and platelet secondary morphologies.



Figure 4. Attempt to fit data from UHMWPE foam from supercritical propane using a 2D platelet model. Micrographs display extremely large crumpled platelets organized into microscale spherical tertiary structures. For the fit t = 354 Å, which agrees with micrographs. XRD peaks are seen at high-q.



Figure 1. SEM micrograph of sample S-3, HDPE 1 (a commercial high density polyethylene with $M_n = 7300$ and $\bar{M}_w = 43000$) (rapid cooling).

Lamellar Structure and Organization in Polyethylene Gels Crystallized from Supercritical Solution in Propane Ehrlich P et al. Macromolecules **24**, 1439-1440 (1991)

SANS from gel versus SAXS from extracted gel.



Figure 9. PAN gels in deuterated solvents and PAN foam display similar morphologies. This indicates that there is little distortion on supercritically drying the PAN gels.



Figure 7. Comparison of the same IPS gel and the corresponding supercritically dried foam. Increase in the slope of the 2D regime indicates densification of the structure. Foam data was previously published.²³

In some cases structure is intransigent

Block Copolymers:

-Single Phase Structure, Thermodynamics

-Microphase separated structure



-BCP micro phase separated structure can be determined using SAXS or SANS (Strobl, G *The Physics of Polymers* Springer Verlag 1997 gives a summary of this topic)

-SANS can be used to measure melt structure and enthalpy of interaction (χ -parameter or A_2)

-SAXS is used to study microphase separated structure

Microphase structure will strongly effect gel properties.



Fig. 3.38. Different classes of microphase-separated structures in block copolymers, as exemplified by polystyrene-*block*-polyisoprene. The numbers give the phase boundaries in terms of the volume fraction of the PS blocks. Figure taken from a review article by Bates and Frederickson [25]

SAXS for microphase separated structure. (Strobl, G *The Physics of Polymers* Springer Verlag 1997)



For spheres you expect HCP Scattering pattern





Fig. 3.39. SAXS curves measured for a series of polystyrene-block-polyisoprenes with different molecular weights in the microphase-separated state: $M = 2.1 \cdot 10^4$, $\phi(PS) = 0.53$ (a); $M = 3.1 \cdot 10^4$, $\phi(PS) = 0.40$ (b); $M = 4.9 \cdot 10^4$, $\phi(PS) = 0.45$ (c) (*left*). Transmission electron micrographs obtained using ultra-thin sections of specimen stained with OsO₄ (*right*). Structures belong to the layer regime. Data from Hashimoto et al. [26]

SANS: BCP' s Single phase and micellar structures.



Figure 1. SANS data of 5 wt $P(EO)_{103}P(PO)_{39}P(EO)_{103}$ in pure D₂O solution at different temperatures. The markers are the experimental data points, and continuous lines are the theoretical fits corresponding to eq 3 for the unimer and eqs 1, 8, and 9 for the interacting micelles.



Figure 3. SANS data of 5 wt % $P(EO)_{103}P(PO)_{30}P(EO)_{103}$ in 0.1 M K₂CO₃ electrolyte solution at different temperatures.

PEO-PPO-PEO block copolymer micelles in aqueous electrolyte solutions: Effect of carbonate anions and temperature on the micellar structure and interaction Sukumaran, Beaucage, Mao, Thiyagaran Macromolecules **34** 552-558 (2001).

Hydrogels: SALS in Water/SANS in D₂O



High-q Helical Polymer Coils in Extended, Linear Conformation (Variation in Helicity with Salt Concentration)

> Intermediate-q Inhomogeneities in Cross-Link Density Yield Statistical Domains of High Crosslink Density (1µm in Size)

Mass-Fractal Network of High Cross-Link Density Domains

> Gel Particles at Lowest-q

Hydrogels: SANS Data in D₂O



Linear, Extended Chains in Swollen State (-1)

Extended Chain Length Varies with Salt Content and Hydrogel Type

> Cross-link Density can be Calculated if Functionality is Known

Helical Coiling may Change with Salt Concentration

Orientation Studies of Nanostructure



Fig. 1. Different orientations of the film: (a) MT orientation, (b) MN orientation, and (c) NT orientation. X indicates direction of the X-ray beam.

We consider 3 orientations and examine HDPE / montmorillonite (quarternary ammonium salt modified) / maleated polyethylene cast films.

A laboratory SAXS camera was used.

SAXS

WAXS (XRD)

A. Bafna et al. / Polymer 44 (2003) 1103-1115



(a) clay clusters/tactoids (0.12 μm),

1107

- (b) modified/intercalated clay stacking period (002) (24-31 Å),
- (c) stacking period of unmodified clay platelets (002) (13 Å),
- (d) clay (110) and (020) planes, normal to (b) and (c),
- (e) polymer crystalline lamellae (001) (190–260 Å), long period¹ and
- (e) polymer unit cell (110) and (200) planes.

Fig. 2. 2-D SAXS ((a) and (c)) and WAXS ((b) and (d)) patterns for orientation MN (left face), NT (right face) and MT (top face) of films HD603 ((a) and (b)) and HD612 ((c) and (d)). The numbers in the parenthesis represent the reflections from the following: (a) clay tactoids, (b) modified/intercalated clay (002) plane, (c) unmodified clay (002) plane, (d) clay (110) and (020) plane, (e) polymer crystalline lamellar, (f) polymer unit cell (110) plane (inner ring) and (200) plane (outer ring).



In I(q) versus q we see two d-spacings in the SAXS regime associated with polymer lamellae and clay d-spacing.

Clay tactoids can be identified.

For XRD (WAXS) we see the clay spacing at low q, clay lateral diffraction peaks, polyethylene unit cell peaks.

Two types of clay are identified.

Fig. 3. (a) SAXS log-log radial plots for clay and HD603, HD612 and HD000 in orientation MN and MT. Here d_c represents the *d*-spacing of the intercalated/modified clay while d_1 represents the *d*-spacing of the polymer lamellar structures in the nanocomposite. (b) WAXS log-linear radial plots for clay and the two films in orientation MT and MN. Here d_u represents the *d*-spacing of the unmodified clay in the nanocomposite.



Orientation can identify the two types of clay, unmodified and modified since they orient in different directions.

This can be seen better in a Stein/Desper plot.

Fig. 4. (a) Azimuthal plot showing the orientation of intercalated clay platelets in HD603 and HD612 in film MN orientation (data averaged from q = 0.15–)30 Å⁻¹). (b) Azimuthal plot showing orientation of unmodified clay, intercalated clay, polymer lamellae and polymer unit cell (110) plane in HD612. The polymer lamellae curve has been truncated owing to the bright anisotropic streak associated with tactoids at 90 and 270° (Fig. 2) as discussed in the text.

85



Normals to planes are plotted using the cosine of the angle to the three priciple sample directions.

Unmodified are identified with

Modified align normal to polymer lamellae.

Fig. 6. Wilchinsky triangle [29-32] for average normal orientation of clay tactoids, unmodified clay platelets, intercalated clay platelets, clay (110)/(020) plane, polymer lamellae (001) and polymer (110) unit cell plane of HD603 and HD612 examined here. For a completely random oriented sample a point in the center results. (- --) Points on this line have their normals randomly arranged in a MT projection. Proximity to ND reflects coplanarity with the MT plane. (----) Points on this line have their normals randomly arranged in the NT projection. Proximity to MD reflects coplanarity with the NT plane.



Fig. 7. Schematic of the orientation of (a) tactoids of modified/intercalated clay platelets, (b) unmodified clay platelets, and (c) polymer crystalline lamellae in the nanocomposite films.

Sodium Laureth-1 Sulfate Surfactant



- Zero-shear viscosity matched
- 1% and 0.25% sodium laureth-1 sulfate (SLE1) in D₂O with NaCI



http://sites.udel.edu/wagnergroup/files/2013/04/couetteshearcell-1.jpg

Prior Rheo-SANS of Branched WLMs

- Published work^{3,4} suggests branching <u>hinders</u> shearalignment
- EHAC surfactant WLMs w/ KCI salt
- A general trend?
- See talk and poster by Calabrese *et al.*
 - Spatially-resolved LAOS
 - Thursday morning



3. Croce et al., Langmuir, **21** (2005) 6762. 4. Qi et al. J. Coll. Int. Sci. **337** (2009) 218.

Radial 2-D Rheo-SANS Patterns (HFIR)



Summary

-SAXS/SANS are useful for a wide range of problems.

-In house instrumentation can be coupled with national and international user facilities under proprietary agreements (\$1,000 range).

-SANS can compliment SAXS and microscopy when contrast enhancement is needed.

-We can categorize SAS measurements according to classes of materials with somewhat different analysis techniques for different classes.







Software for My Collaborators/Students (And Me)

All Methods are available in Jan Ilavsky's Igor Code http://www.uni.aps.anl.gov/usaxs/

Anomalous Scattering



All Methods are available in Jan Ilavsky's Igor Code http://www.uni.aps.anl.gov/usaxs/

Unified Fit (Not all implemented)



All Methods are available in Jan Ilavsky's Igor Code http://www.uni.aps.anl.gov/usaxs/

Sphere (or any thing you could imagine) Distributions



All Methods are available in Jan Ilavsky's Igor Code http://www.uni.aps.anl.gov/usaxs/

Maximum Entropy/Regularization Code (Jemian)

