Material Characterization at Nano Order Length Scale -A SAXS Study

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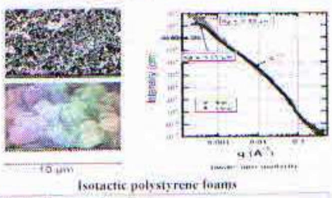
Scattering vs Imaging: Discover the Similarity



Isotactic polystyrene foams

Scattering methods

- Neutron Scattering - scatter from nucleus, element sensitive
- X-rays scatter off of all the atoms/particles in the sample (sensitive to electron density difference)

- The scattered waves interfere, which produces distinct spots or rings at specific angles...

$$n\lambda = 2d\sin\theta$$

Small Angle Scattering

$$q = 4\pi\frac{\sin(\theta)}{\lambda} \qquad d = \frac{2\pi}{q}$$

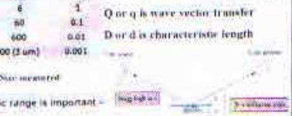
1	0.6	10
0.1	6	1
0.01	60	0.1
0.001	600	0.01
0.0002	3000 (3 um)	0.001

Q or q is wave vector transfer

D or d is characteristic length

Size measured

Detector dynamic range is important - Intensity ~ q^{-4}



Examples of Scattering

Multiple length scales. Complimentary methods are helpful

Prevailing length scale in the system

Oriented sample. Can find orientation direction and degree of orientation

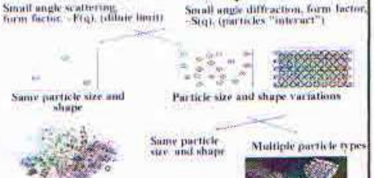
- Large dynamical range of scattering
- Not necessarily a specific features are present
- Integration and background corrections needed

Small Angle Diffraction Well defined periodic nanostructures

SAXS is a broad range of methods *type of information it can provide*

Small angle scattering, form factor - F(q), (dilute limit)

Small angle diffraction, form factor -S(q), (particles "interact")



Same particle size and shape

Particle size and shape variations

Same particle size and shape

Multiple particle types

Measurement in SAXS

Measured quantity

Dilute = independent scatterers = NO interparticle effects
Total intensity = sum of individual particle scattering

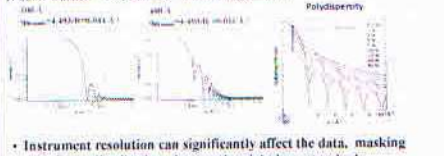
$$I(q) \propto \frac{N}{V} V^2_{particle}(\rho - \rho_s)P(q)S(q)$$

P(q) = Form factor - SHAPE and SIZE information P(q) is dimensionless and P(0) = 1

** In the literature, as in this presentation, both P(q) and F(q) are commonly used symbols for form factors*

Effect of Particle Size and Polydispersity

(volume fraction = 1%, contrast = 10^{10} A^{-2}, bkgd = 0.01)

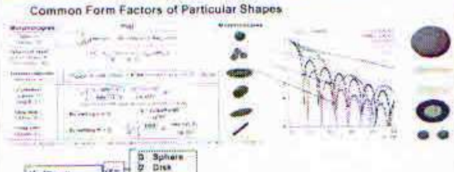


- Instrument resolution can significantly affect the data, masking "true" size distribution, the sample might be not so bad (polidisperse) as it might look
- Resolution should be accounted to separate effect of polydispersity

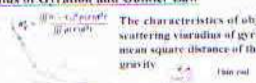
Scattering from Individual Shaped Objects

Common Form Factors of Shaped Objects (many more were computed numerical)

Common Form Factors of Particular Shapes



Radius of Gyration and Guinier Law



The characteristics of objects are encoded in the low -q scattering via radius of gyration (Rg) calculated as the root mean square distance of the object's parts from its center of gravity

$$R_g^2 = \frac{3}{5}R^2 \qquad R_g^2 = \frac{L^2}{12} \qquad R_g^2 = \frac{R^2}{2} \qquad R_g^2 = \frac{d^2}{8} + \frac{L^2}{12}$$

Sphere, Thin rod, Thin disc, Cylinder

- Guiner Law allows finding R_g without any model assumption
- The Guinier region of the scattering data would not be linear if sample contains aggregation

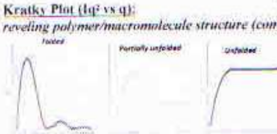
Guinier Law Examples

Deviant Guinier Plots aren't necessarily 'bad' as they tell you something about the state of the macromolecule in solution

BSA Examples 1) Aggregated 2)good data 3) inter-particle repulsion

Kratky Plot (Iq^2 vs q):

reveling polymer/macromolecule structure (compactness)



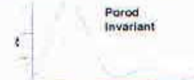
- Compact (i.e. folded) macromolecules exhibit a bell-shaped curve in a Kratky Plot – I(q) vs. q^2, I(q) vs. q^2
- Extended (i.e. unfolded) macromolecules have plateau at higher q

(Plot Iq^2 vs. q. Differentiation between folded and unfolded protein)

Kratky Plot examples: Lysozyme
1)Folded 2) Partially folded (8 M urea)
3)Partially folded (90° C)
4)Unfolded (8 M urea at 90° C)

- Porod invariant, Q, is the integral of the area of the Kratky curve

$$Q = \int_0^\infty I(q)q^2dq$$



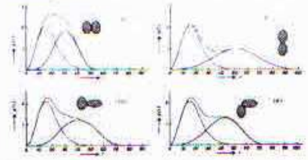
Q is a concentration independent value and is proportional to molecular mass.

Distance distribution function

P(r): distance distribution function is related to the frequencies of distances within particle

$$P(r) = r^2\int_0^\infty I(q)\frac{\sin(qr)}{qr}4\pi q^2 dq$$

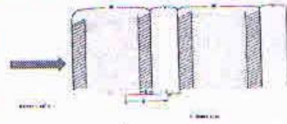
- Calculation of *P(r)* from
- data in limited q-range requires specialized algorithm

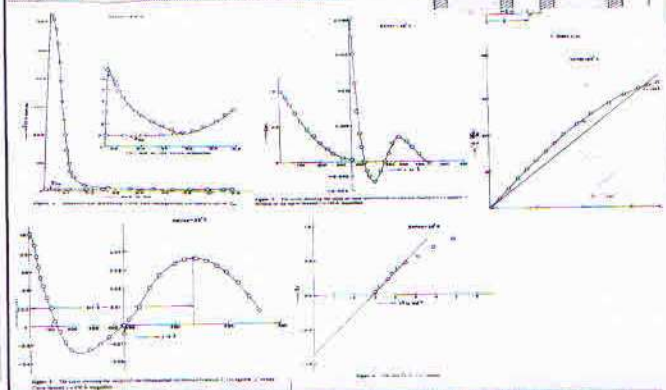


Deriving Information from SAXS Data

Glatter and Kratky Small Angle X-ray Scattering

Application to Cellulose Macromolecules





SAMPLE	D (nm)	S/V(nm^{-1}) x10^{-2}	E (nm)	Φ_1(%)	Φ_2(%)	σ
jute	61.6	32.5	3.2	82	18	0.171
sisal	91.1	21.9	2.2	86	14	0.150
cotton	51.7	38.7	3.0	79	21	0.181

Cocluding Remark

- The SAXS study of the above mentioned three air dried plant fibers i.e. jute, sisal and cotton fibers were made to evaluate the relevant parameters using suitable theory and the results shows that the cellulose macromolecules are more closely packed in cotton fiber in comparison to jute and subsequently to sisal.
- This closely packing behavior of cellulose macromolecules enhances various properties of cotton fiber in comparison to that of jute and sisal fibers.
- Hence, especially in developing fiber reinforced composites (FRP) cotton possesses better compatibility with the polymer matrix in comparison to that of jute and least compatibility with that of sisal fiber.

References

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