Small Angle X-Ray Scattering:

What information can you get from this technique?

Industry event
7th May 2015

NCD beamline at ALBA

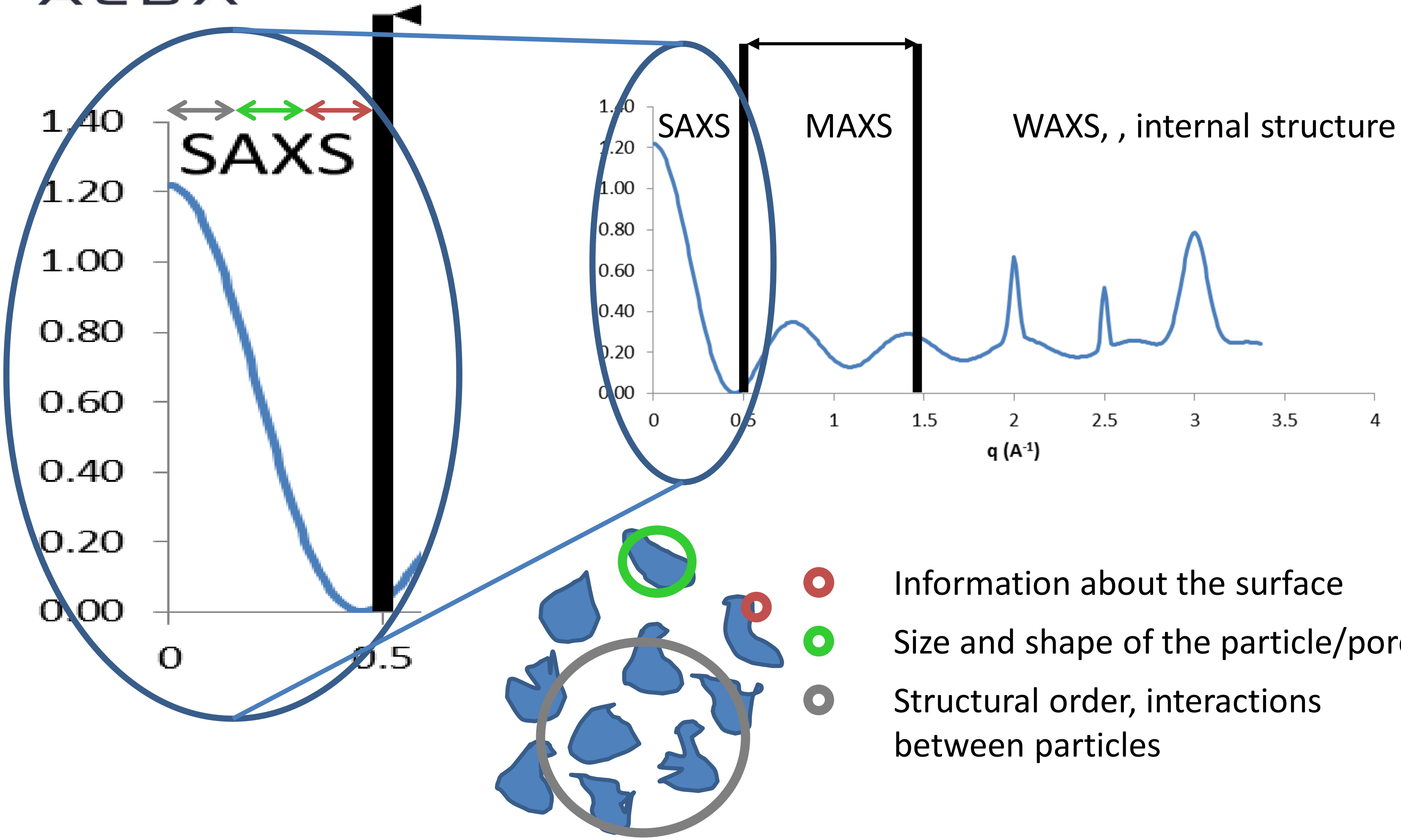
A wide range of fields:

- Medicine
- Biology
- Chemistry
- Physics
- Archaeology
- Environmental and conservation sciences
- Materials

A wide range of systems:

- Polymer processing
- Self assembly of mesoscopic metal particles
- Colloids
- **Cements**
- **Pigments**
- **Ceramics**
- **Glasses**
- Liquid crystals
- Corneal transparency

What do we measure?



- Information about the surface
- Size and shape of the particle/pore
- Structural order, interactions between particles

Only synchrotron gives access to the different modes

Cement

The mechanical properties (Strength and Elasticity)

Continuous reaction of water with the cement.

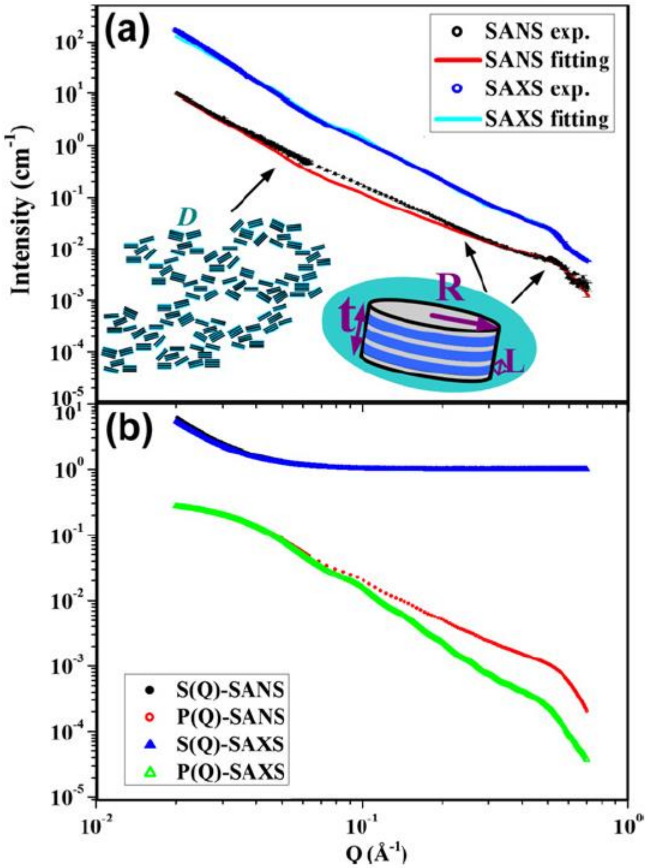
This hydration process can last for several years.

Strongly affected by additives

Chiang W. et al, Journal of Colloid and Interface Science 398 (2013) 67–73

Cement

Microstructural changes of globules in calcium–silicate–hydrate gels with and without additives determined by small-angle neutron and X-ray scattering



Parameters extracted from the model fitting of SAXS and SANS data.[a]

Sample	L_{SAXS} (Å)	L_2 (Å)	$\bar{n}$	R (Å)	D
CSH	13.05(3)	4.46(5)	0.85(1)	59.31(8)	2.81(1)
CSH + PCE23-2	12.06(1)	4.4(1)	2.46(1)	104.1(1)	1.67(1)
CSH + PCE23-6	12.36(1)	4.80(4)	1.48(1)	59.08(8)	2.62(1)
CSH + PCE102-2	12.76(3)	4.20(7)	1.01(1)	58.92(8)	2.70(1)
CSH + PCE102-6	12.54(1)	4.46(5)	1.48(1)	66.7(1)	2.68(1)

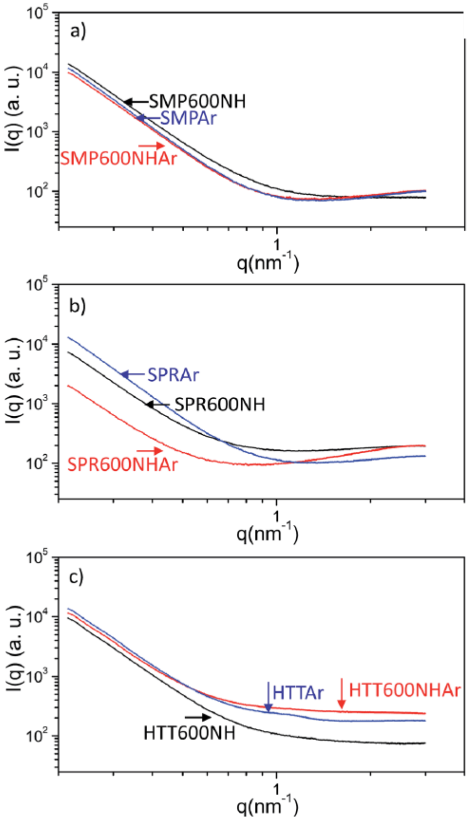
Conclusion from the article

rately. We demonstrated, for the first time, that PCE additives can enhance the local stacking of the calcium silicate sheets through increasing the average number of repeating layers in the globules,

Chiang W. et al, Journal of Colloid and Interface Science 398 (2013) 67–73

Ceramics

NH_3-assisted synthesis of microporous silicon oxycarbonitride ceramics from preceramic polymers: a combined N_2 and CO_2 adsorption and small angle X-ray scattering study†



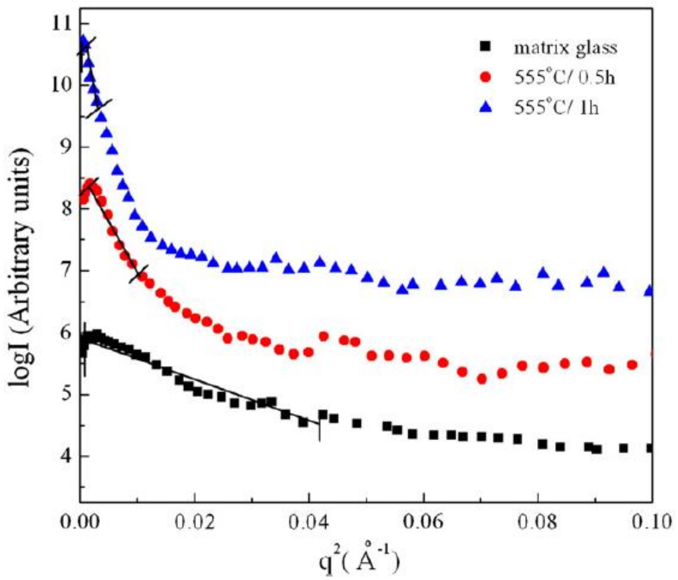
Sample	$S^{BET}_{CO_2}$ ($m^2 g^{-1}$)	$S^{D-A}_{CO_2}$ ($m^2 g^{-1}$)	$V^{t-N_2}_{micro}$ ($cm^3 g^{-1}$)	V^{D-A,CO_2}_{micro} ($cm^3 g^{-1}$)	$V^{N_2}_{T}$ ($cm^3 g^{-1}$)	D–A exponent	D–A energy (kJ mol^{-1})	d_{D-A} (nm)	R^{av}_g (nm)	n
SMP600NH	—	—	—	—	—	—	—	—	0.12	3.5
SMP600NHAr	6	50	0	0.03	0.02	1.17	3.9	2.2	No Guinier range	3.3
SMPAr	—	—	—	—	—	—	—	—	No Guinier range	3.7
SPR600NH	240	310	0.21	0.15	0.28	1.54	6.0	1.4	No Guinier range	3.6
SPR600NHAr	270	416	0.16	0.18	0.18	1.82	8.5	0.8	No Guinier range	3.7
SPRAr	—	—	—	—	—	—	—	—	No Guinier range	3.8
HTT600NH	357	641	0.13	0.26	0.14	1.85	11.5	0.5	0.20	3.5
HTT600NHAr	279	426	0.14	0.17	0.16	2.07	11.0	0.5	0.20	3.4
HTTAr	57	68	0	0.03	0.02	1.97	10.2	0.6	0.50	3.5

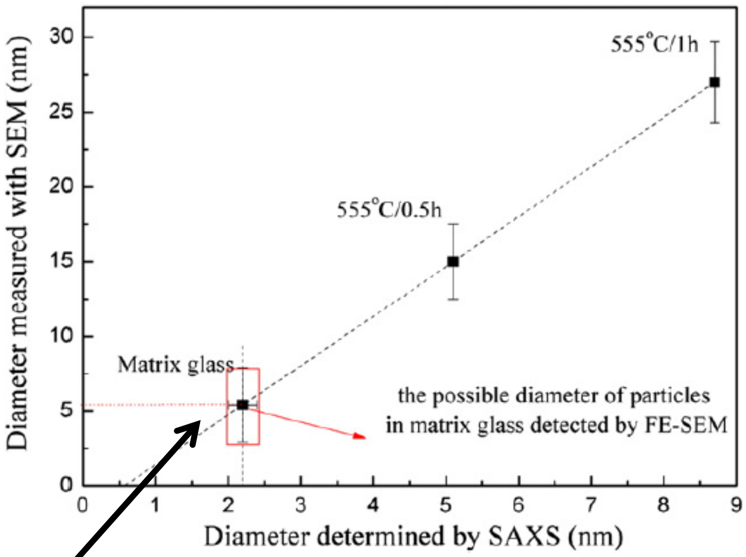
under an Ar atmosphere at 750 °C. Under these synthesis conditions polysiloxane (SPR-212a, Starfire® Systems) and polysilazane (HTT-1800, KiON Specialty Polymers) transform to microporous ceramics, while materials derived from polycarbosilane (SMP-10, Starfire® Systems) remain non-porous, as revealed by N_2 and CO_2 adsorption isotherms. Small angle X-ray scattering (SAXS) characterization indicates that samples prepared from polycarbosilane possess latent pores (pore size < 0.35 nm) which are not accessible in the gas adsorption experiments. The microporous silicon oxycarbonitride (SiCNO) ceramics synthesized from polysilazane and polysiloxane by the above-mentioned route possess a

Schitco C. et al, J. Mater. Chem. A, 2015, 3, 805

Glass Ceramics

Liquid-phase separation and crystallization of high silicon canasite-based glass ceramic





Not detectable by FE-SEM, limit of the technique resolution

Pigments

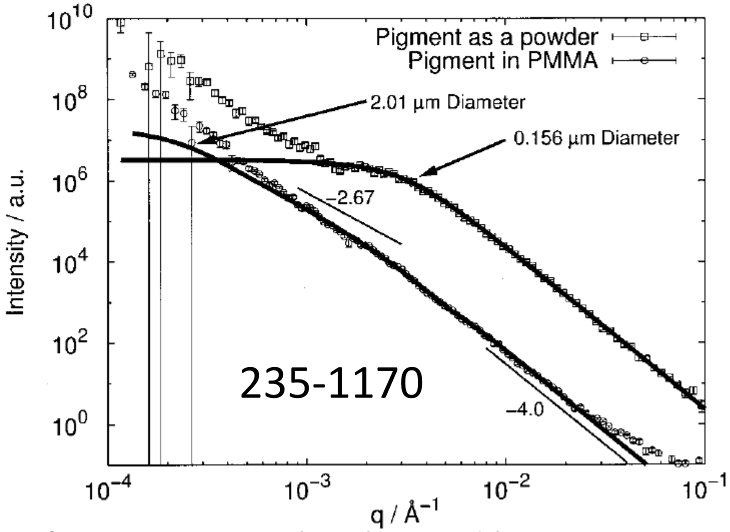
Relation of the fractal structure of organic pigments to their performance

Different pigments:

Pigment Red 170, 235-0170

Pigment Red 170, 235-1170

embedded in polymer matrices



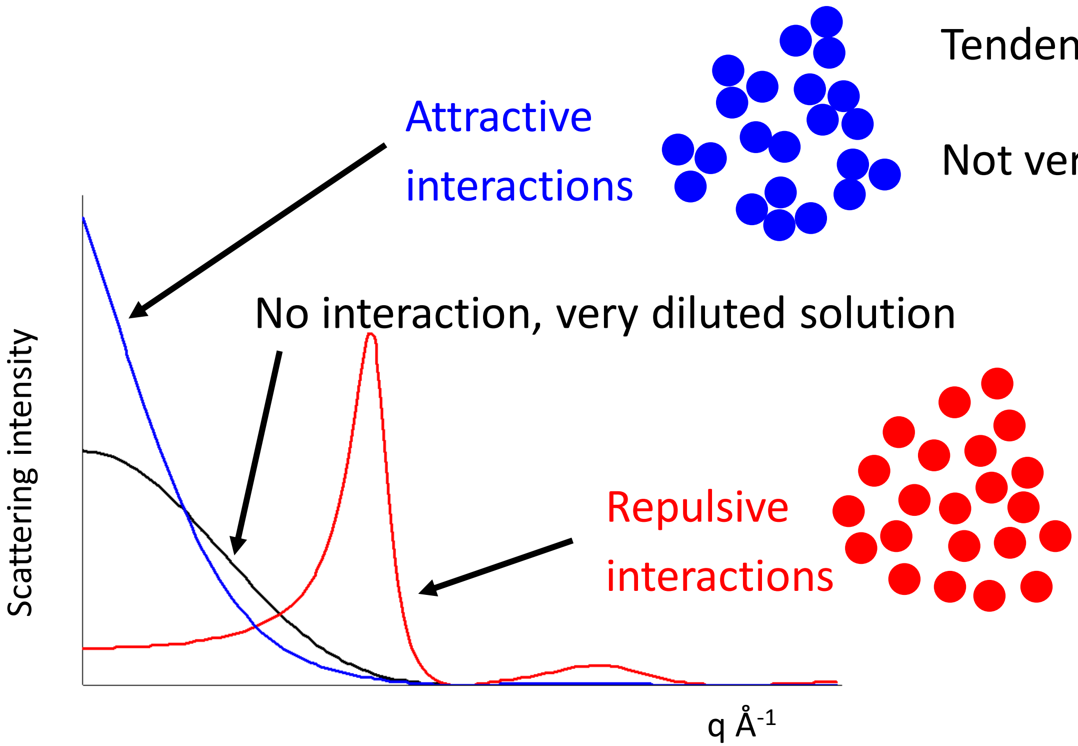
IV. CONCLUSIONS

- Organic pigments display aggregation behavior.
- The size change of the pigment particles and the formation of aggregates can be observed by SAXS.
- No chemical change in the pigments and no change in the crystalline phase is observed on mixing in the polymer.
- The size of the formed aggregates has a strong effect on the light scattering properties of the embedded pigments. Thus small differences in size have an effect noticeable by visual observation on the color brilliance (chroma). From this effect an optimum primary pigment particle size distribution can be deduced, so that a minimal amount of pigment will yield the most brilliant color possible. An alternative method would be to add surface active agents to control aggregation or particles with the same refractive index as the matrix, which can prohibit the pigment particles clustering together.

Skillas G. et al, Journal of Applied Physics **91**, 6120 (2002); doi: 10.1063/1.1466524

Pigments

Typical curves of scattering intensity



Tendency to form aggregates

Not very good for painting

System sterically stabilised

Better for painting

Conclusion

SAXS techniques gives information on:

- Structural parameters of ceramics, glasses and advanced materials
- Particle shape analysis and particle size distribution information can be obtained for colloidal suspensions;
- Phase behaviour in self-assembled systems such as paints, cosmetics and detergents.