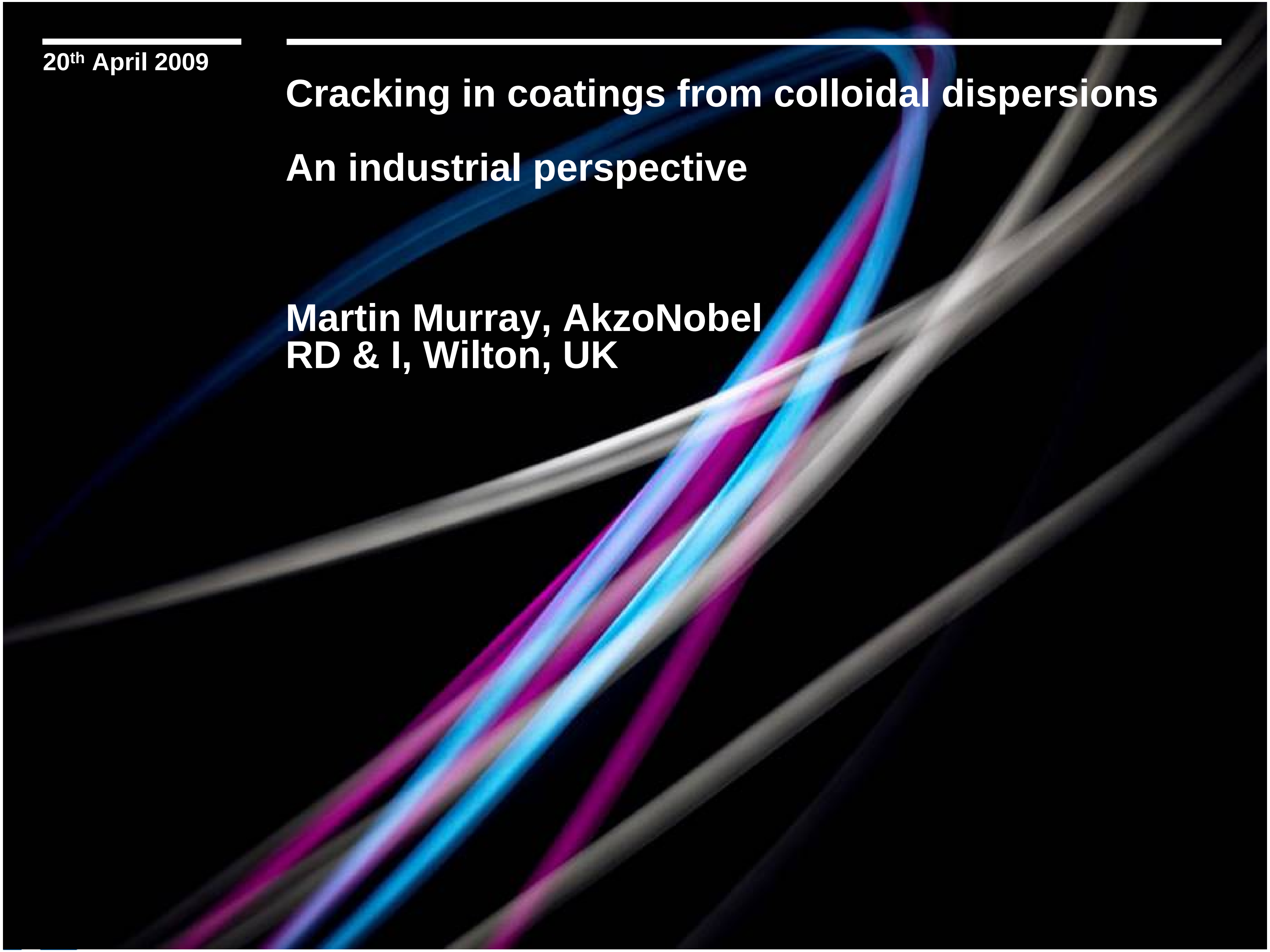

20th April 2009

Cracking in coatings from colloidal dispersions

An industrial perspective

Martin Murray, AkzoNobel
RD & I, Wilton, UK

Overview

- Acknowledgements
- Introduction to “mud-cracking”
- Why is AkzoNobel concerned with cracking?
- Cracking development during drying
- Theoretical considerations of cracking
- Drying stress
- Influence of drying rate
- Influence of specific surface area
- Particle blends
- Conclusions

Acknowledgements

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- Prof. Lee White, Prof. Mahesh Tirumkudulu, Dr Alex Routh

Gerrards Cross village pond
Summer 2006

Gerrards Cross village pond circa 1960

Sahara desert – photo taken during 2007 Marathon De Sables

Why is AkzoNobel concerned with cracking?

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Why is AkzoNobel concerned with cracking?

- Significant proportion of AN’s business is within the coatings sector
- Cracking restricts the available formulation space

- Cracking specifically becomes an issue as we;
    - Drive cost reduction whilst maintaining performance
    - Reformulate to meet legislative drive for VOC reduction
    - Reduce binder levels to increase “sustainability”

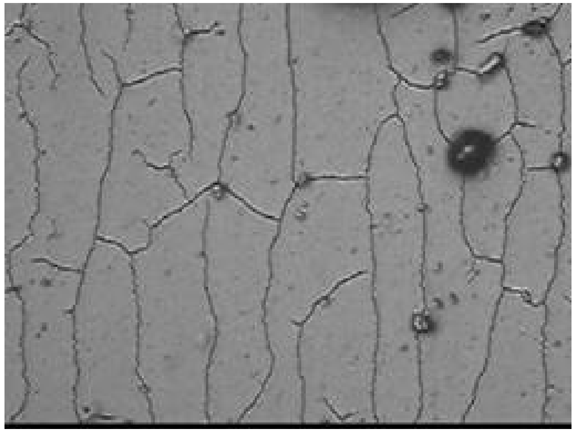
- Cracking impacts upon product performance;
    - Aesthetic appearance of decorative paints
    - Mechanical properties and integrity
    - Transport/barrier properties in general

Why is AkzoNobel concerned with cracking?

When it all goes wrong…………

Why is AkzoNobel concerned with cracking?

More typical examples of the problems caused by cracking



Cracking of conductive tracks produced by printing dispersions of silver nano-particles

Cracking in decorative paints

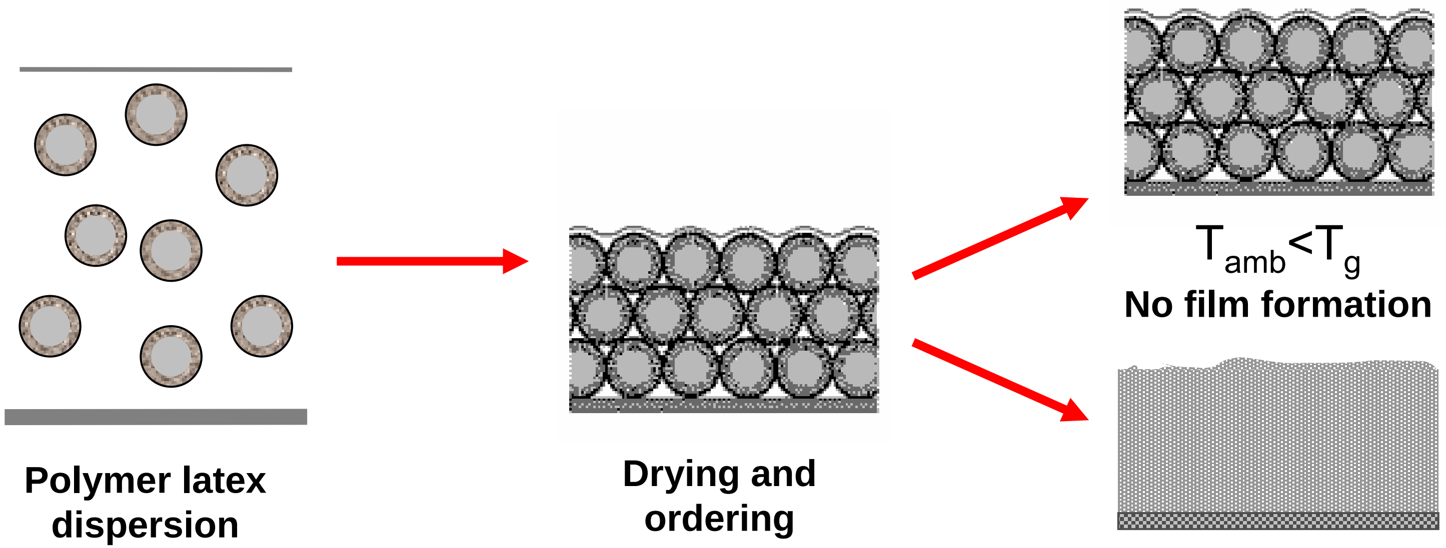
Curling of a flexible substrate induced by drying stress

Restriction of the available formulation space

Consider the role of VOC’s in waterborne paints

Latex film formation process

- Good film properties depend upon latex coalescence
- Latex coalescence depends upon polymer $T_g < T_{amb}$



Polymer latex dispersion

Drying and ordering

$T_{amb} < T_g$

No film formation

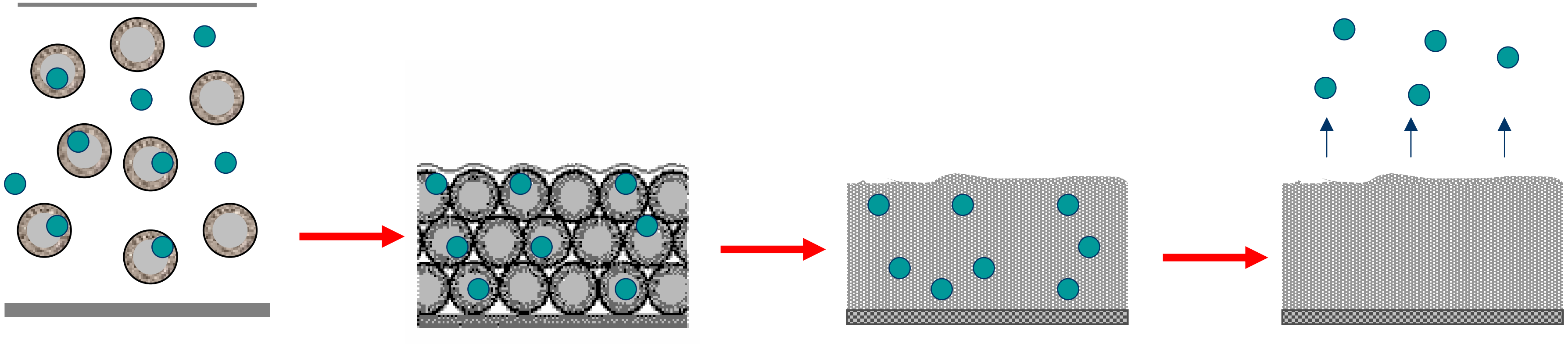
$T_{amb} > T_g$

Film formation

Restriction of the available formulation space

Polymer T_g is reduced by added VOC's (volatile plasticisers)

Loss of VOC's post film formation to regain T_g



Polymer latex dispersion

Drying and ordering

Film formation

$T_g < T_{amb}$

Loss of VOC's

$T_g \sim T_{amb}$

"Soft" polymer phase helps to control the drying stresses

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Why is AkzoNobel concerned with cracking?

- Removing VOC's from w/b paints introduces several challenges
- Not least of which is controlling the cracking

- Using a softer polymer is not an option in most applications
  - Introduces blocking/dirt pick up issues

- Legislative pressure to reduce solvents within paints (2007/2010)

- Routes to low and zero solvent containing paints have to maintain the property balance whilst addressing the cracking

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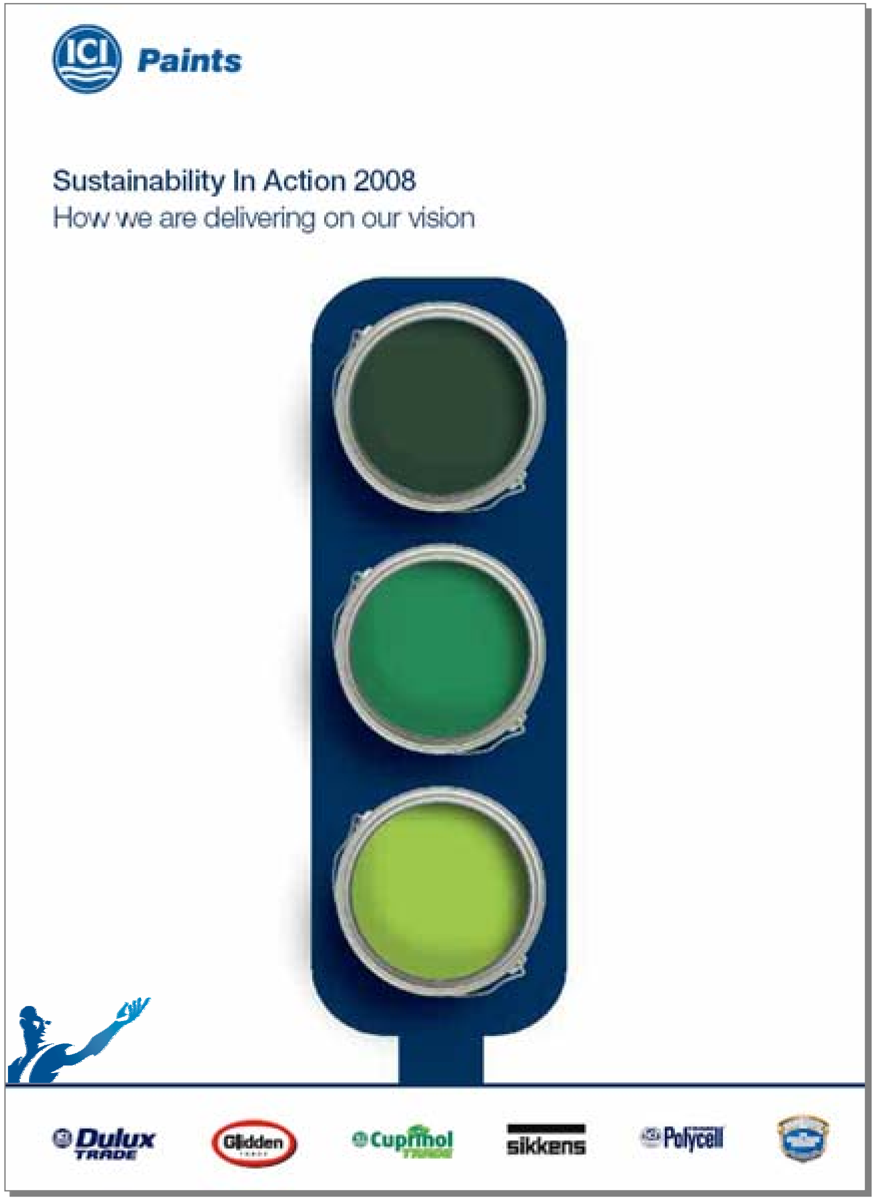
Why is AkzoNobel concerned with cracking?



ICI Paints

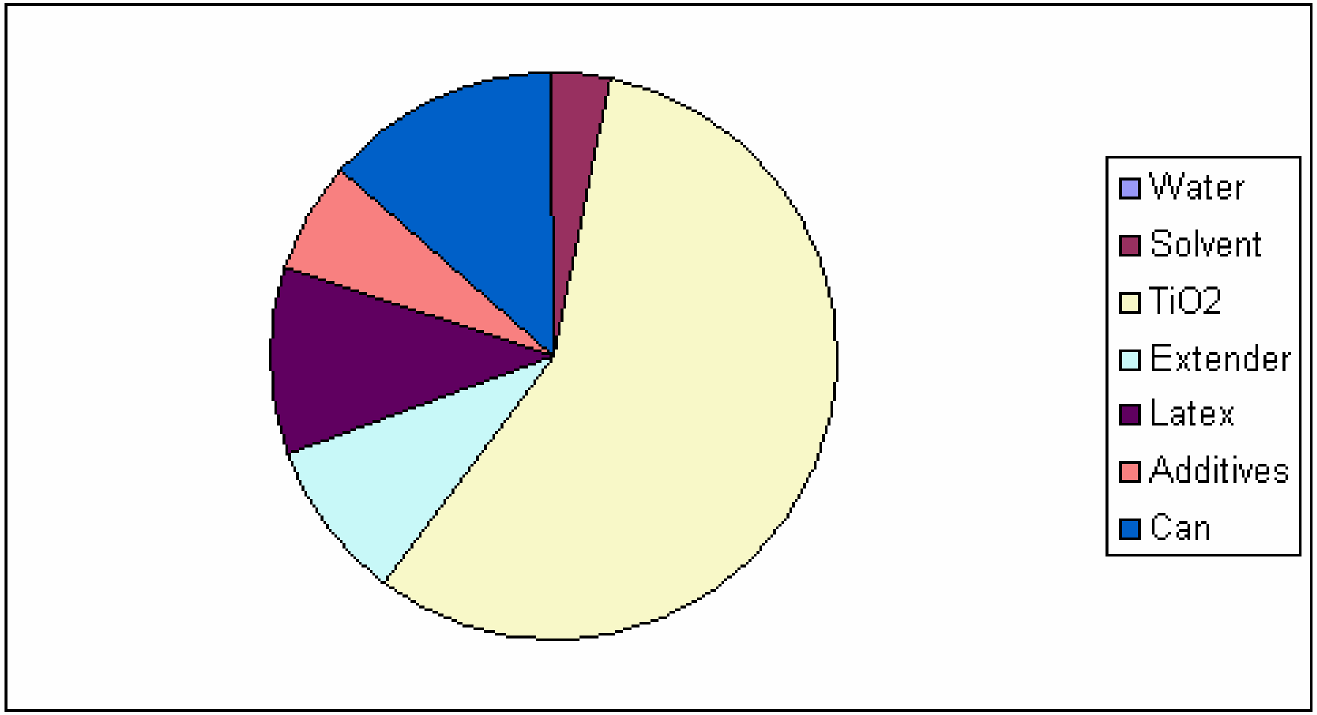
Sustainability In Action 2008
How we are delivering on our vision

Dulux Trade · Glidden · Cuprinol Trade · sikkens · Polycell

- Sustainability has become a key driver in many business sectors
- Decorative paints is no exception
- Removal of solvents is just one aspect of this driver
- Sustainability forces one to consider the whole supply chain

Why is AkzoNobel concerned with cracking?

Relative contribution to the carbon footprint of the components in a typical matt paint



The latex forms a significant part of the embodied carbon in a can of paint
It also consumes “non-renewable” petrochemicals feedstock
Reducing latex levels in paints makes a positive contribution to “sustainability”
However it will also compromise the ability of the paint to resist cracking

Our approach

step
towards
greener

Which means…

- We are on a journey and we are serious about it
- Open and honest approach
- With Integrity

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Tomorrow's Answers Today

Summary

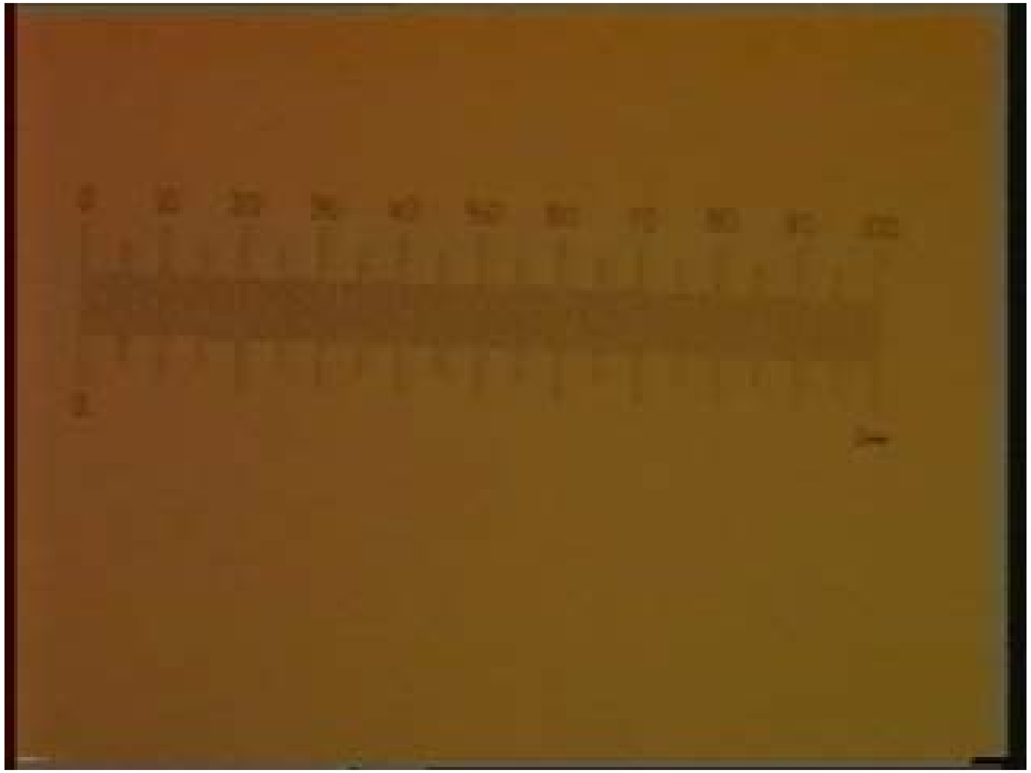
- Cracking imposes restrictions on our formulation space
- It limits our ability to formulate solvent-free, more sustainable and cheaper products

- Developing a comprehensive understanding of the factors that control and govern cracking is important for the realisation of next generation products
- A critical step in this journey is to understand how the individual components contribute to crack behaviour

Cracking development during drying

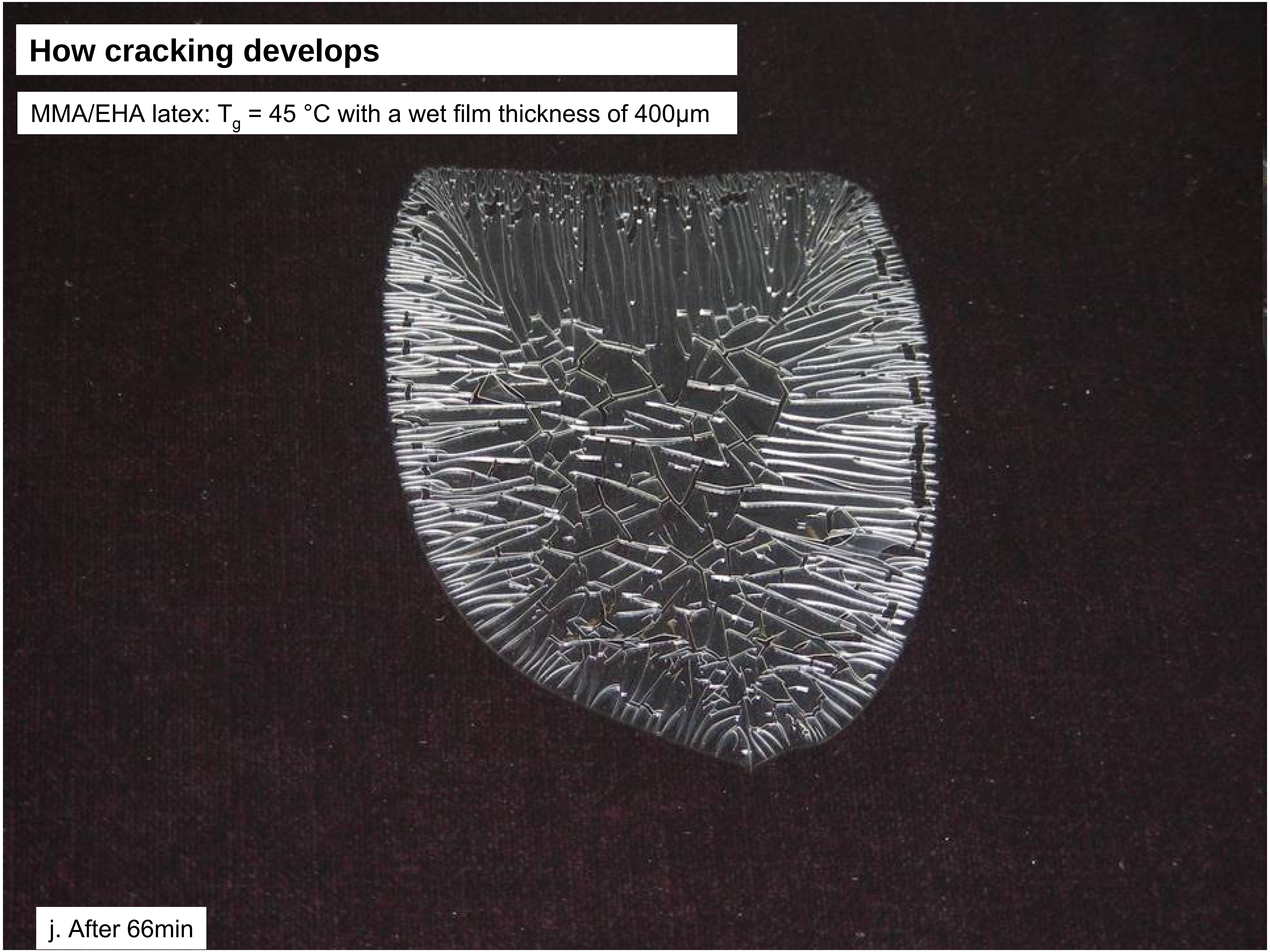
Cracking development during drying

Drying and cracking of an aqueous pyrogenic silica dispersion

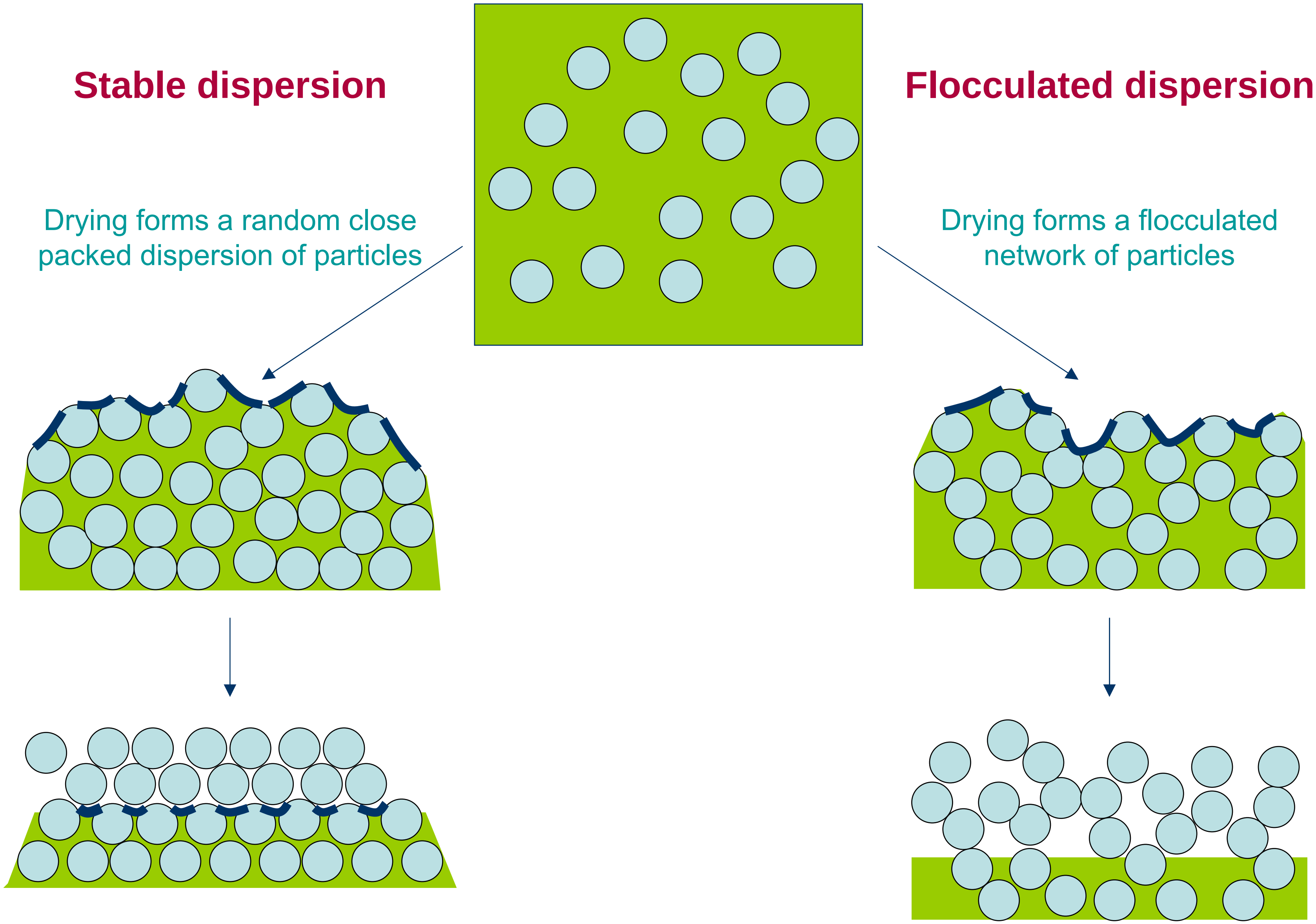


How cracking develops

MMA/EHA latex: T_g = 45 °C with a wet film thickness of 400μm



j. After 66min



Stable dispersion

Drying forms a random close packed dispersion of particles

Capillary pressure compresses the particle network causing densification

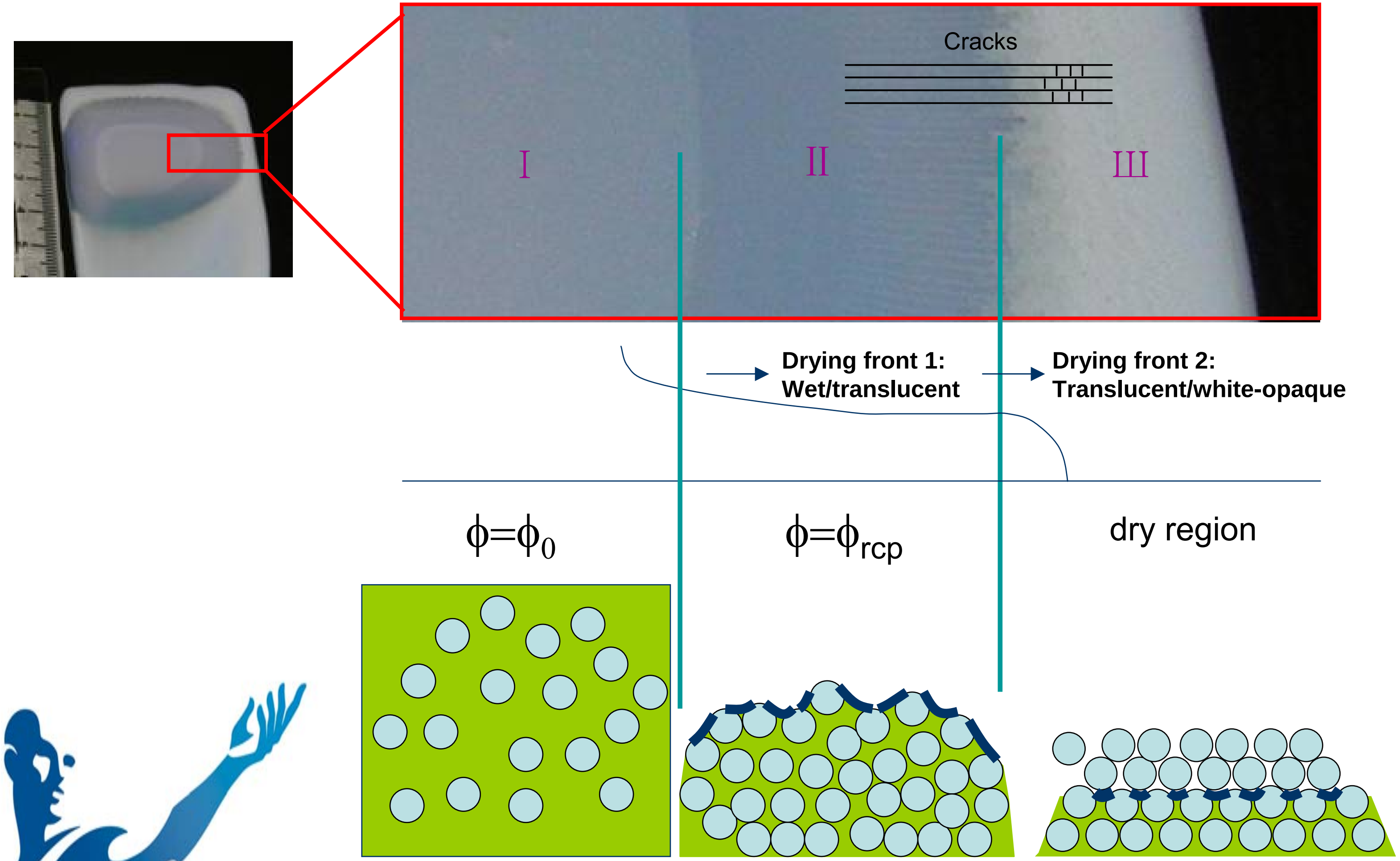
Flocculated dispersion

Drying forms a flocculated network of particles

Particle network strength is greater than the compressive stress induced by capillary pressure and a porous coating results

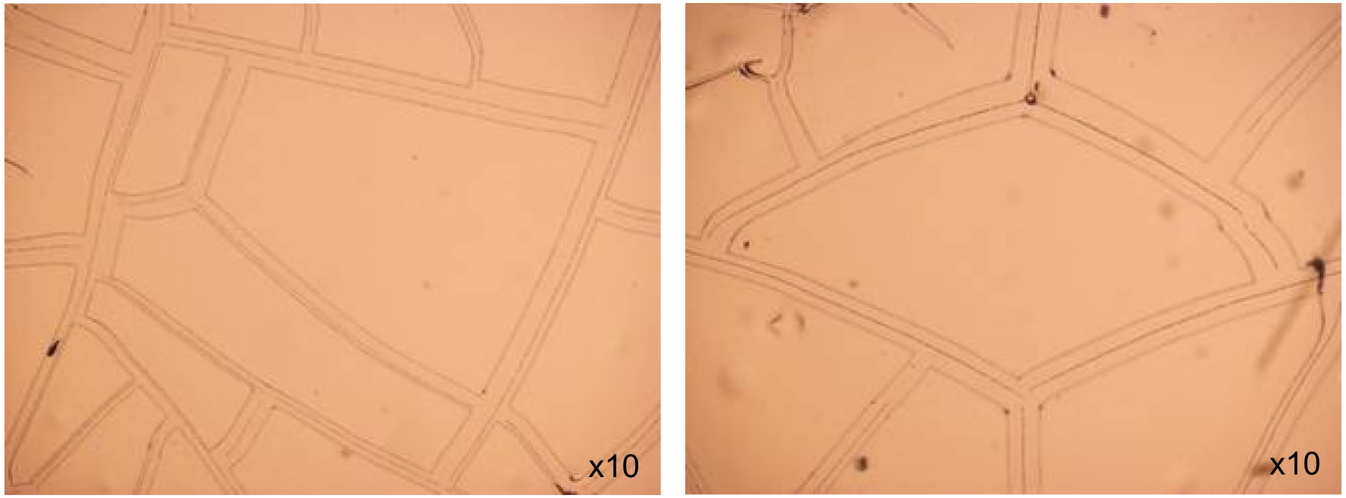
Cracking development during drying

Typically observe 3 “discreet” regions during drying



A critical observation is that the cracks run into the “wet” region

Cracking development during drying



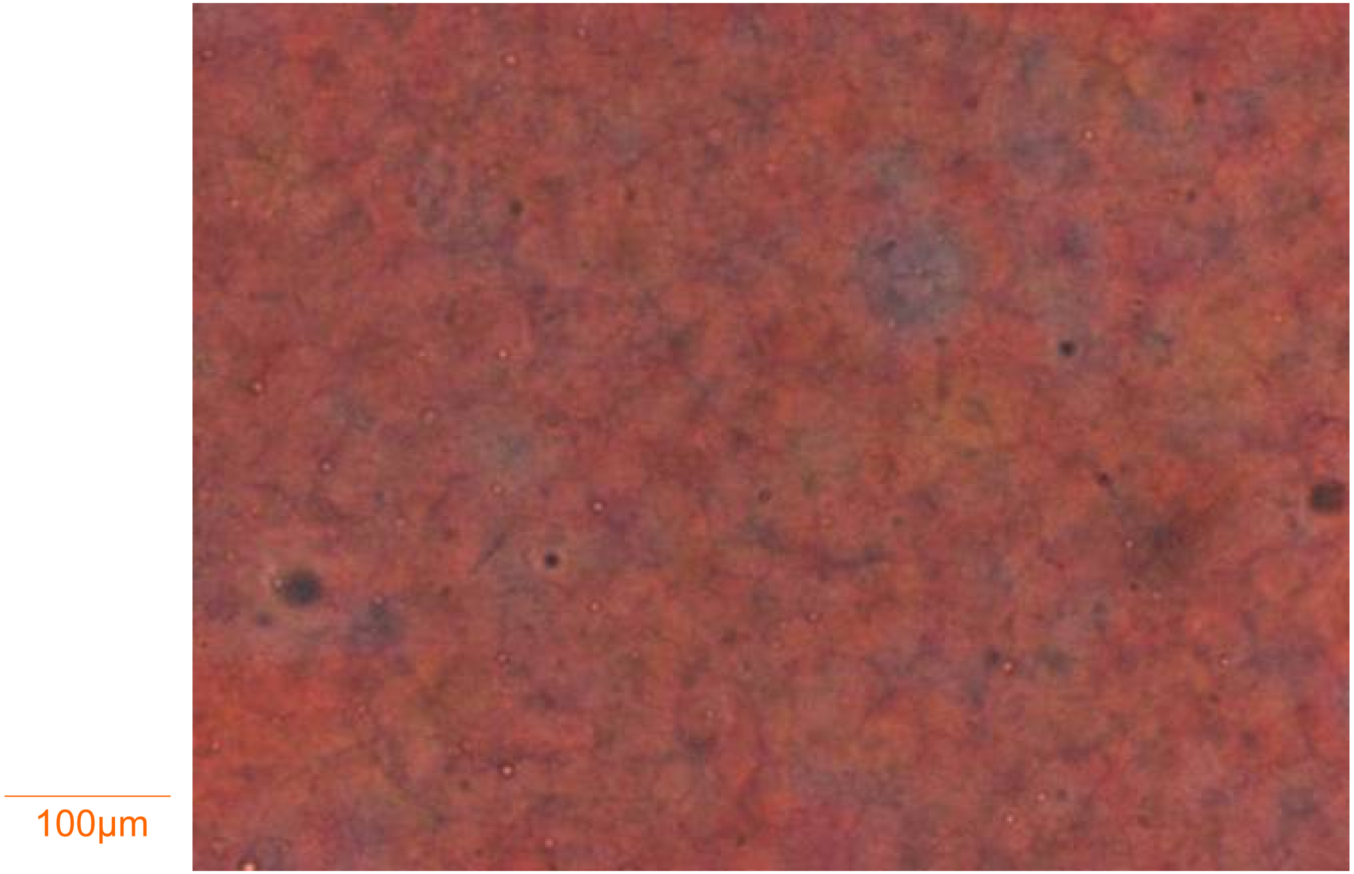
In some systems a trace of particles is left at the initial cracking point

This allows an estimate of the volume shrinkage after cracking

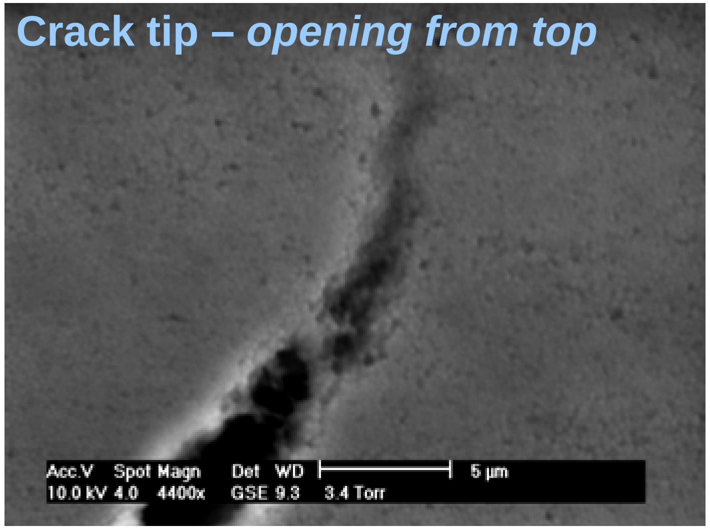
In stable systems this typically equates to around 20-30vol%

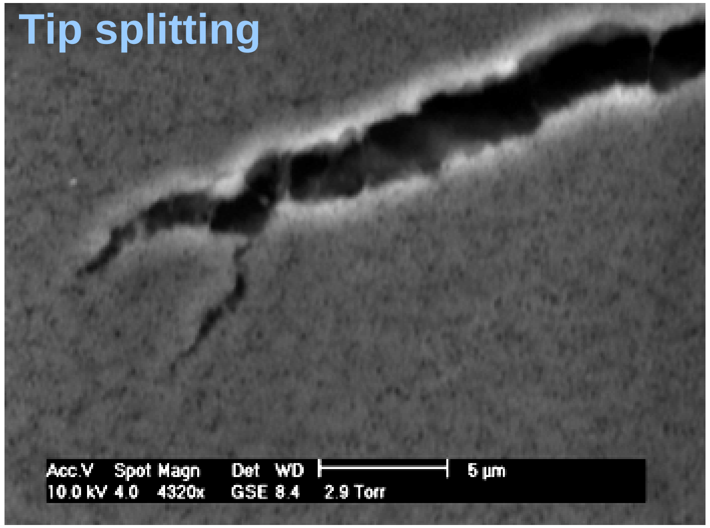
Cracking development during drying

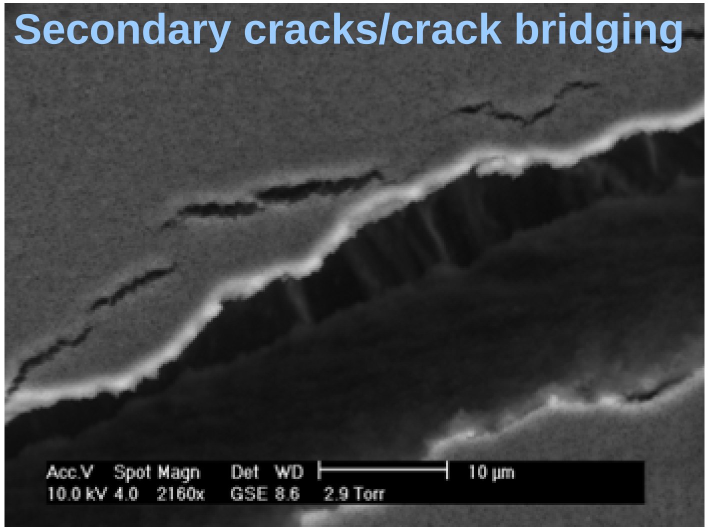
Drying and cracking of an aqueous latex dispersion (T_g ~30°C)



ESEM images of crack formation


Crack tip – *opening from top*


Tip splitting


Secondary cracks/crack bridging

These images provide insight into how cracks first develop

Cracks open up from the top of the coating to the bottom

It is necessary for a network to exist for crack propagation

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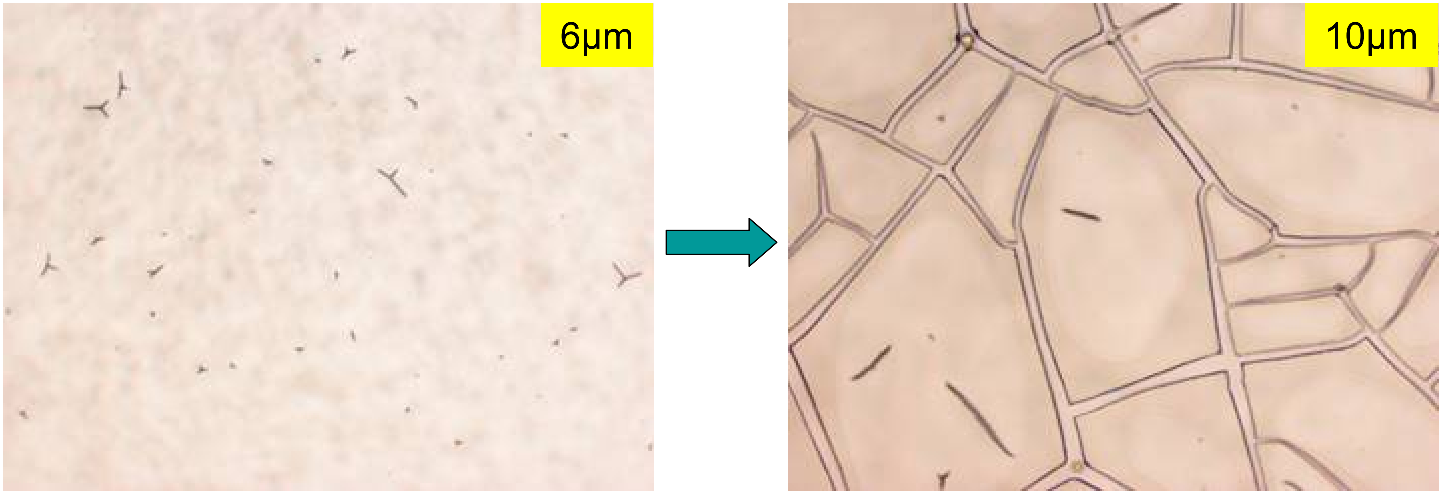
Critical cracking thickness (CCT)

For any given formulation that is prone to cracking there will be a coat thickness below which no cracking is observed

Microscope images of dried films of a high T_g latex

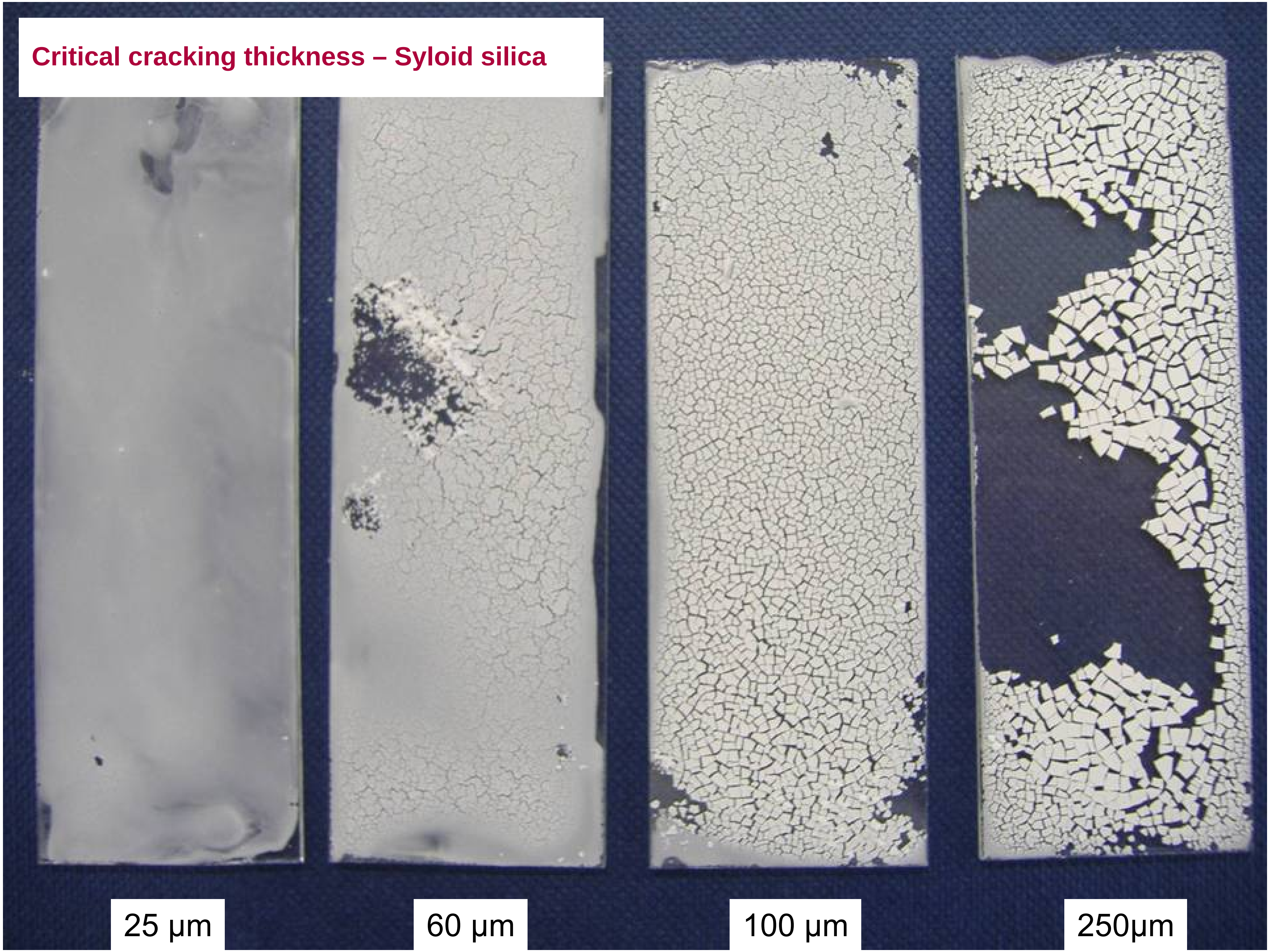


Below critical coat thickness

Above critical coat thickness

Much of our work has concentrated on understanding on how to maximise the CCT

Critical cracking thickness – Syloid silica

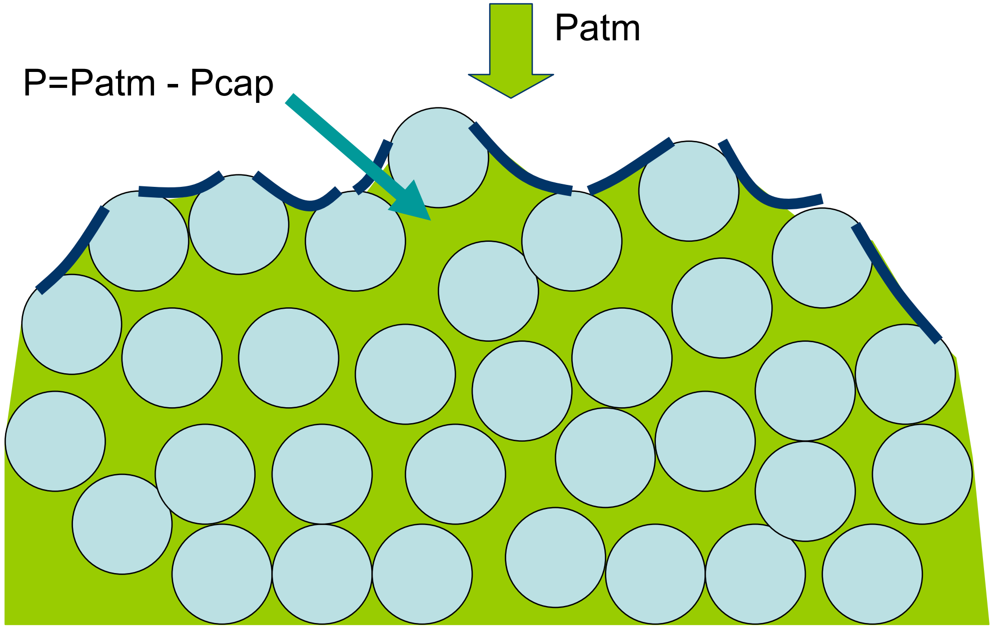


Summary

- Both inorganic and “hard” organic particulate dispersions are prone to cracking
- Crack propagation appears to follow the drying fronts within a coating
- Cracks run from the dry region into the saturated, networked region of the coating
- For any given colloidal dispersion there is a breakpoint with increasing coating thickness from crack free to cracked – the so called critical cracking thickness

Theoretical considerations of cracking

The importance of the capillary pressure



$$P_{cap} = \frac{\Sigma \gamma \cos \theta \phi}{(1-\phi)}$$

LR White, J.Colloid Sci. 90, 536 (1982)

Σ = surface area/unit volume of solid

γ = surface tension

θ = contact angle

ϕ = particle volume fraction

The capillary pressure arises due to dewetting of the particles by the liquid – this generates a negative pressure in the fluid

The capillary pressure puts the particle network into compression and therefore the liquid into tension – it is this that causes the coating to crack

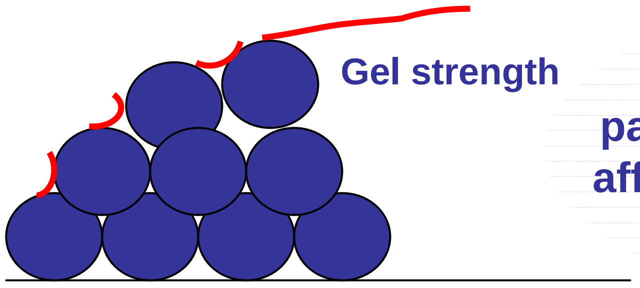
For soft particles, e.g. low T_g polymer latices, it is the capillary pressure that causes particle deformation and closure of voids within the coating

Influence of particle size on P_{cap}

Particle radius	P_{cap} (bar)
1 μm	1
100 nm	10
10 nm	100

approx. maximum capillary pressure at $\phi = 0.64$ for monodisperse spheres in water

Cracking style and critical cracking thickness



The balance of capillary pressure, particle network strength and substrate affinity determine the cracking style and critical cracking thickness

The above considerations determine when and how the solid phase "sets up" and begins to support stress elastically, especially in a flocculated system

How does a system resist the imposed shrinkage strain due to drying?

Griffiths fracture criterion

- From the available data (see later);

$$\mathrm{CCT} \propto \mathrm{P}_{\mathrm{cap}}^{-1.8} \propto \Sigma^{-1.8}$$

- If we were dealing with a linear, elastic solid film then the usual way of explaining this relationship would be to balance the elastic energy release rate with the rate of increase in surface energy
- Doing so gives an exponent of -2
- We, however, are dealing with a wet film comprising particles
- The case of a porous film comprising deformable particles has been considered by Russel & Tirumkudulu who find an exponent of -1.5

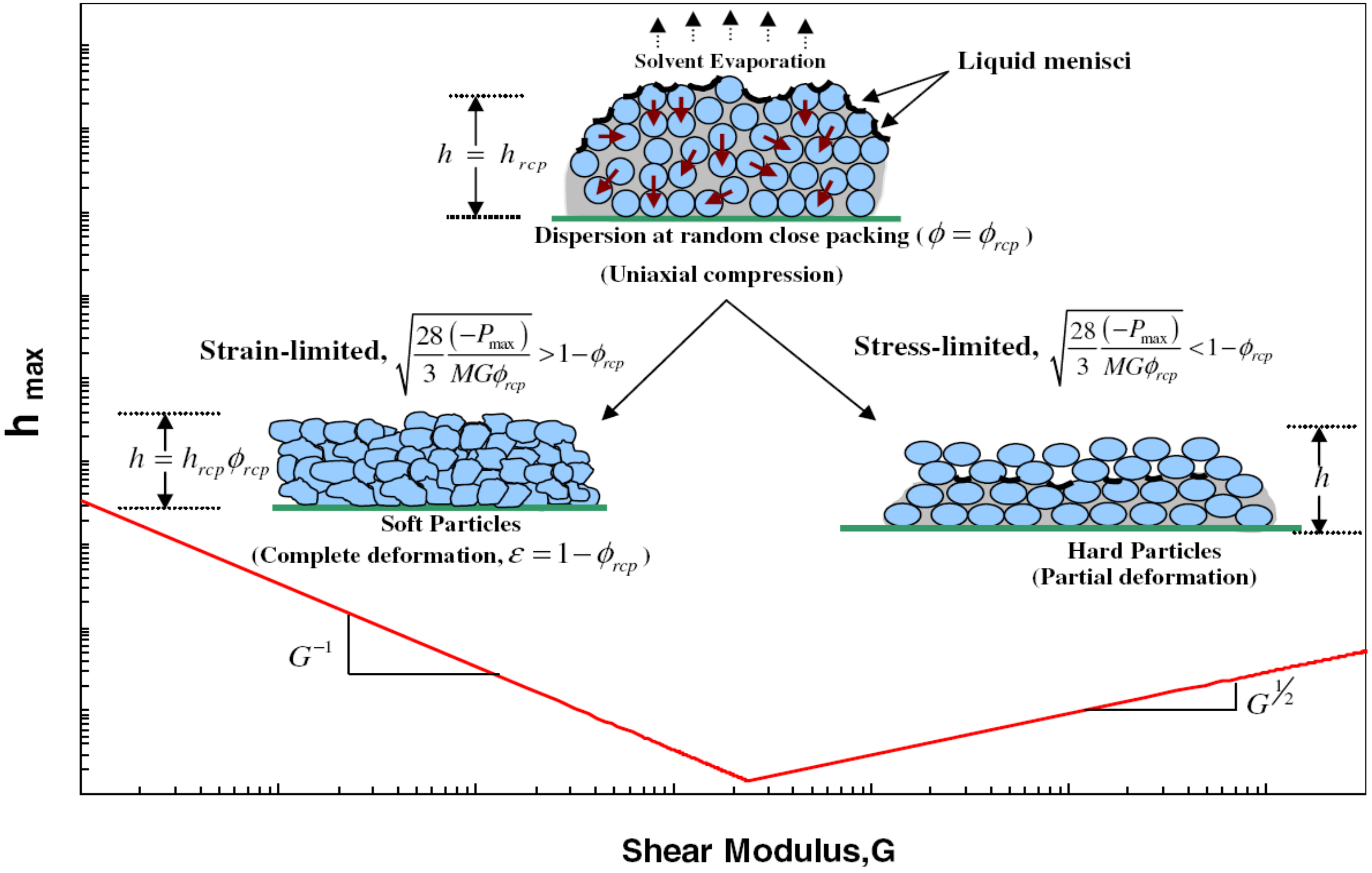
Theoretical considerations of cracking

- Tirumkudulu et al. have gone on to derive a relationship to describe the CCT
- For hard particles this critical thickness is dependent upon;
  - the shear modulus of the particles (G)
  - the maximum capillary pressure ($-P_{max}$)
  - the solvent-air interfacial tension
  - the co-ordination number (M)
  - the particle volume fraction (Φ_{rcp}) and particle size (R)

$$CCT = 0.64\left[\frac{GM\Phi_{rcp}R^3}{2\gamma}\right]^{1/2}\left[\frac{2\gamma}{(-P_{\max})R}\right]^{3/2}$$

Singh, Tirumkudulu – PRL **98**, 218302 (2007)

Critical Cracking Thickness regimes



Singh, Tirumkudulu – PRL **98**, 218302 (2007)

Summary

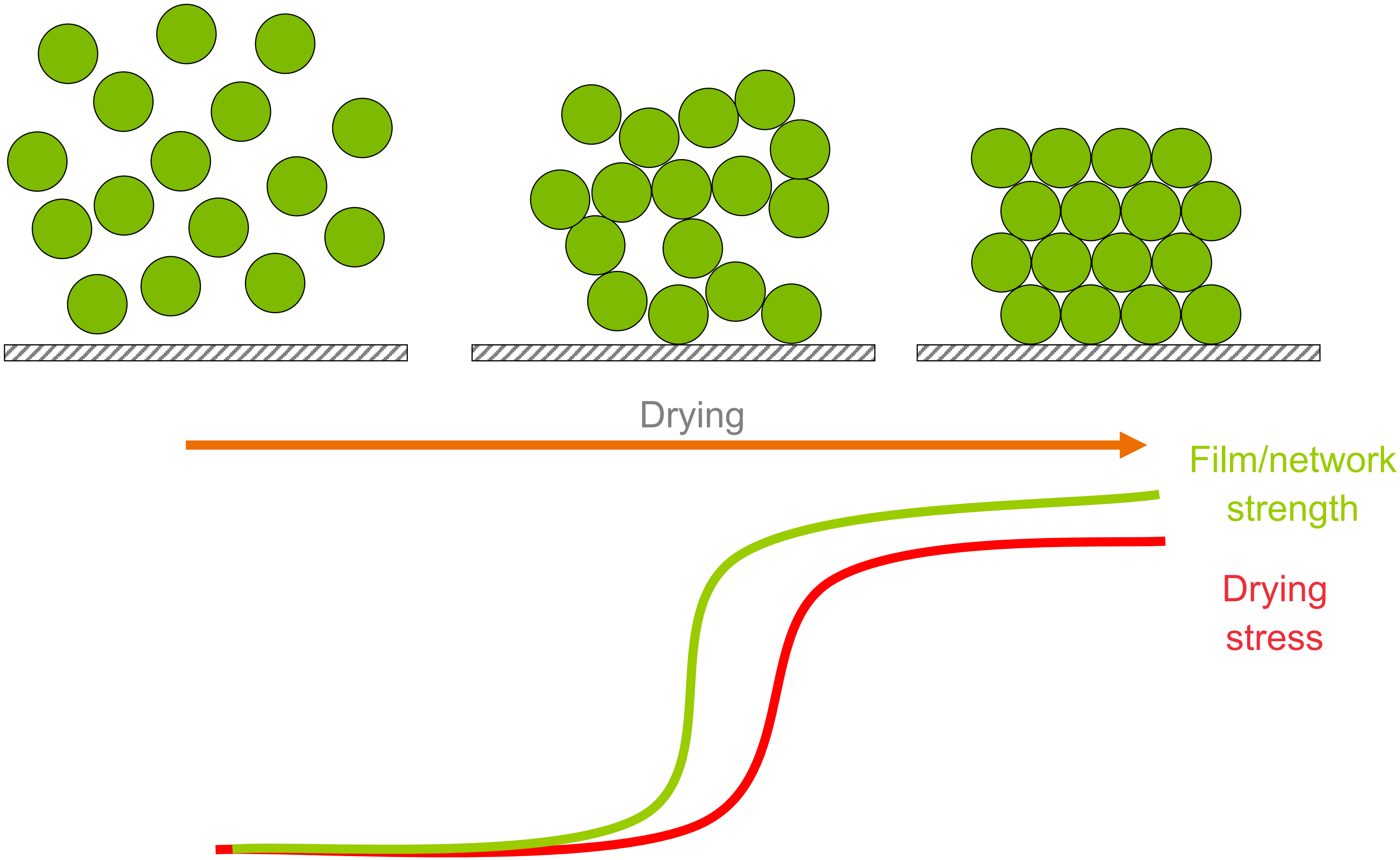
- The theory of cracking during drying of particulate dispersions has made great strides over the past decade or so
- Ultimately it is the capillary pressure generated during the drying that is responsible for cracking
- How the capillary pressure is balanced against the particle network strength and the affinity of the coating for the substrate will determine if and how the coating will crack
- The problem can be addressed by Griffiths fracture criterion which suggests a correlation between the capillary pressure and the coating thickness at which cracking is observed
- Recent theory developments suggest approaches that might be taken to reduce or eliminate cracking in coatings

Drying stress

Drying stress

- Stress is caused by dimensional changes occurring within the coating as it is losing volume and becoming anchored to the substrate
- Measuring the instantaneous drying stress within a coating has been tackled by cantilever beam methods
- Due to inhomogeneous drying, driven by edge drying, what is measured is an averaged drying stress
- Coupled with gravimetric data such measurements can provide insight into stress growth and relaxation processes and the factors that influence them

Drying stress

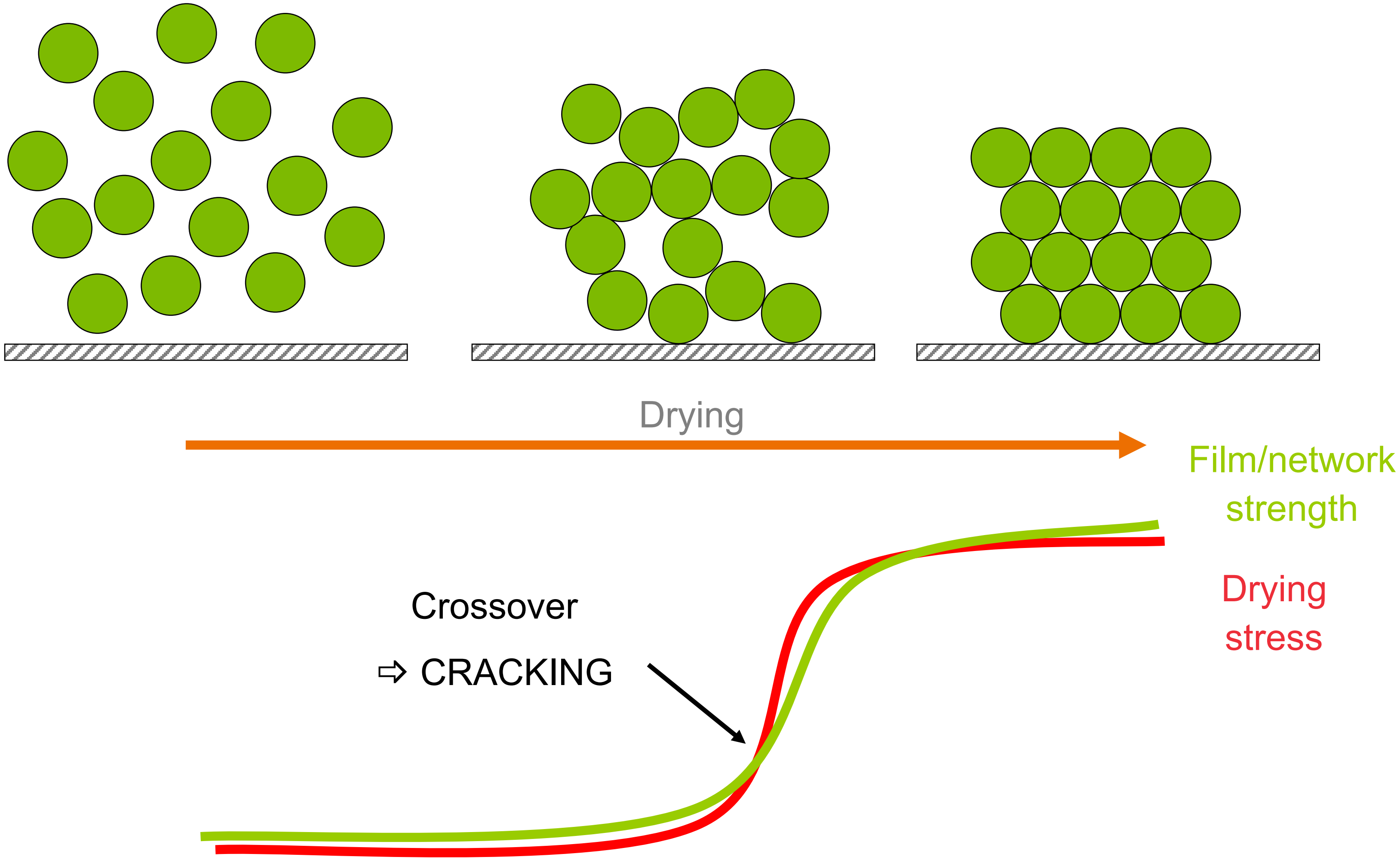


Drying

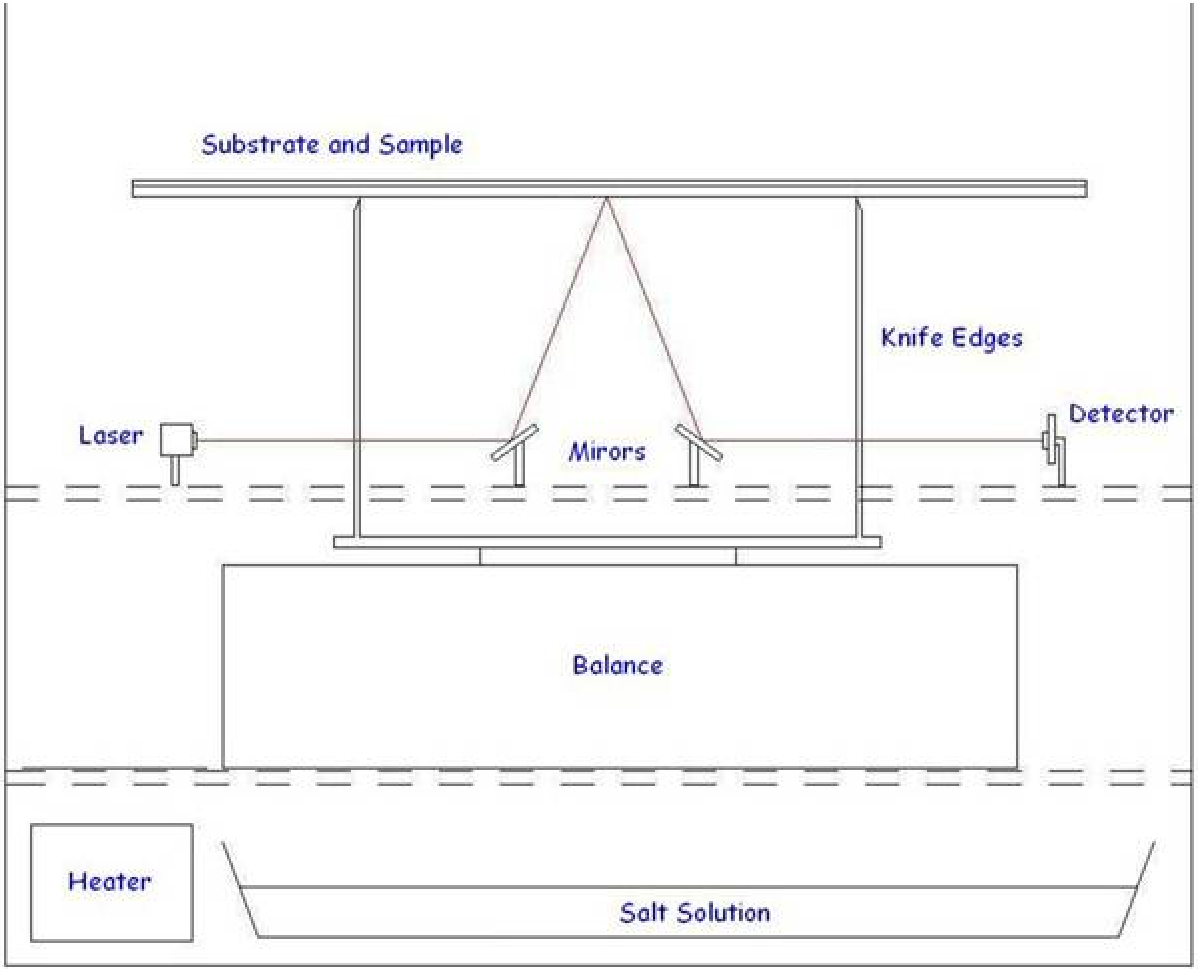
Film/network strength

Drying stress

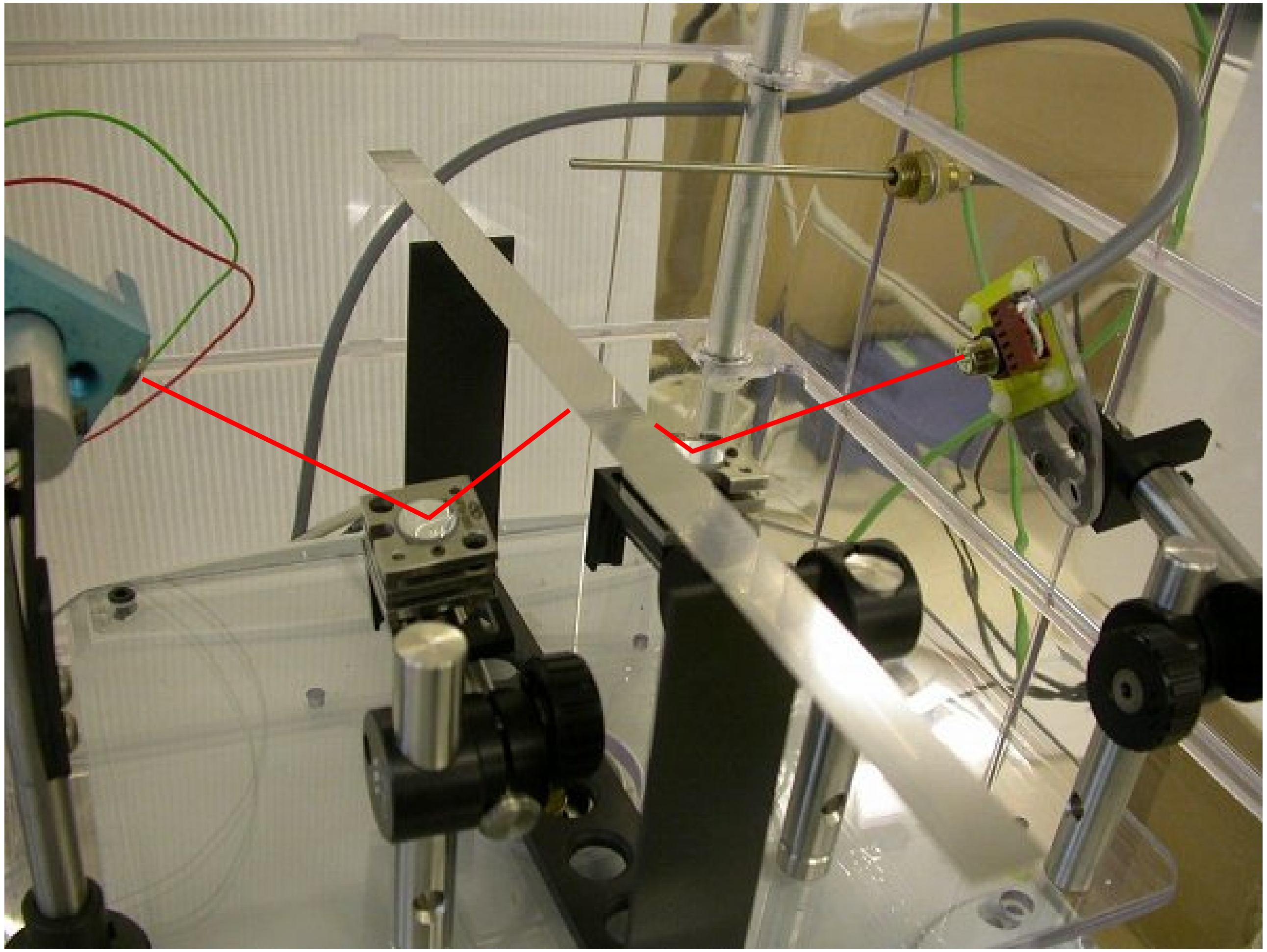
Drying stress



Measuring the drying stress



Measuring the drying stress



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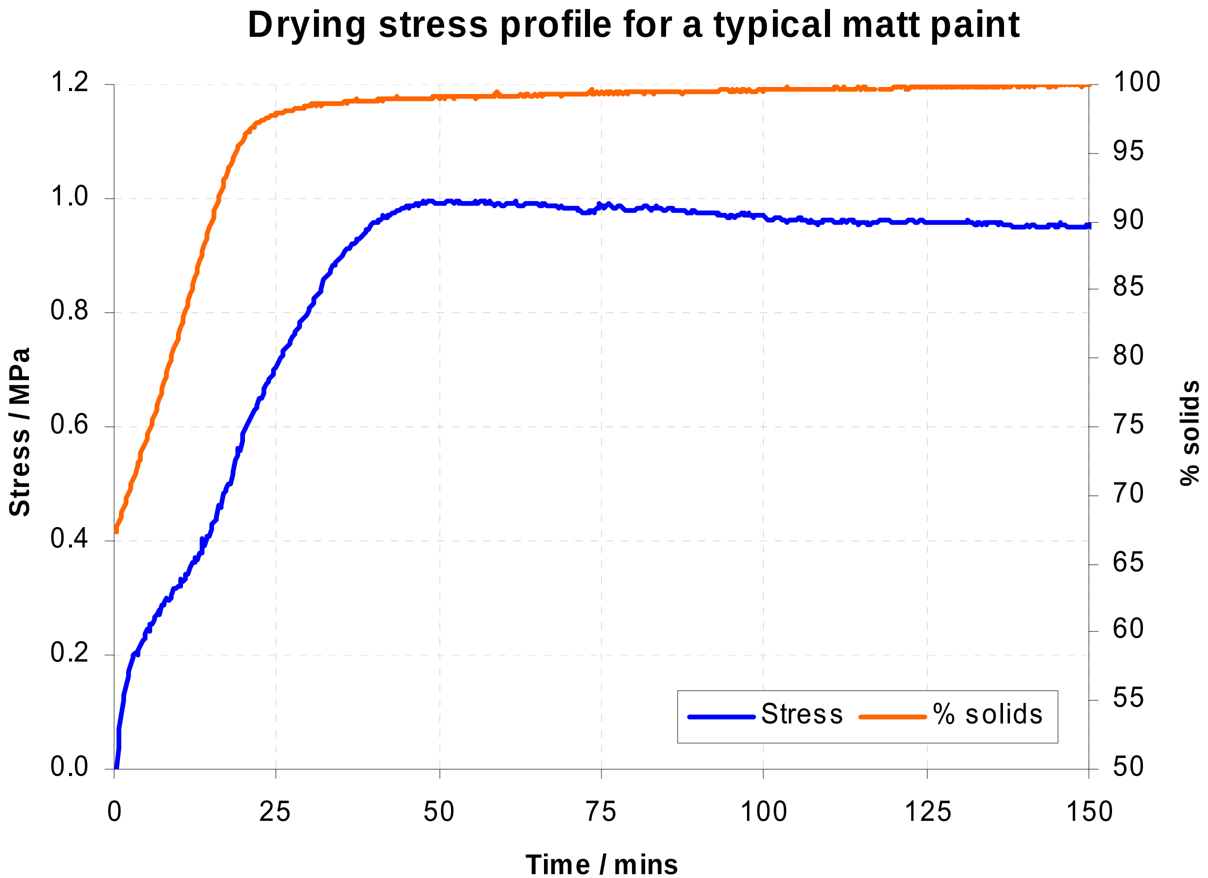
Measuring the drying stress

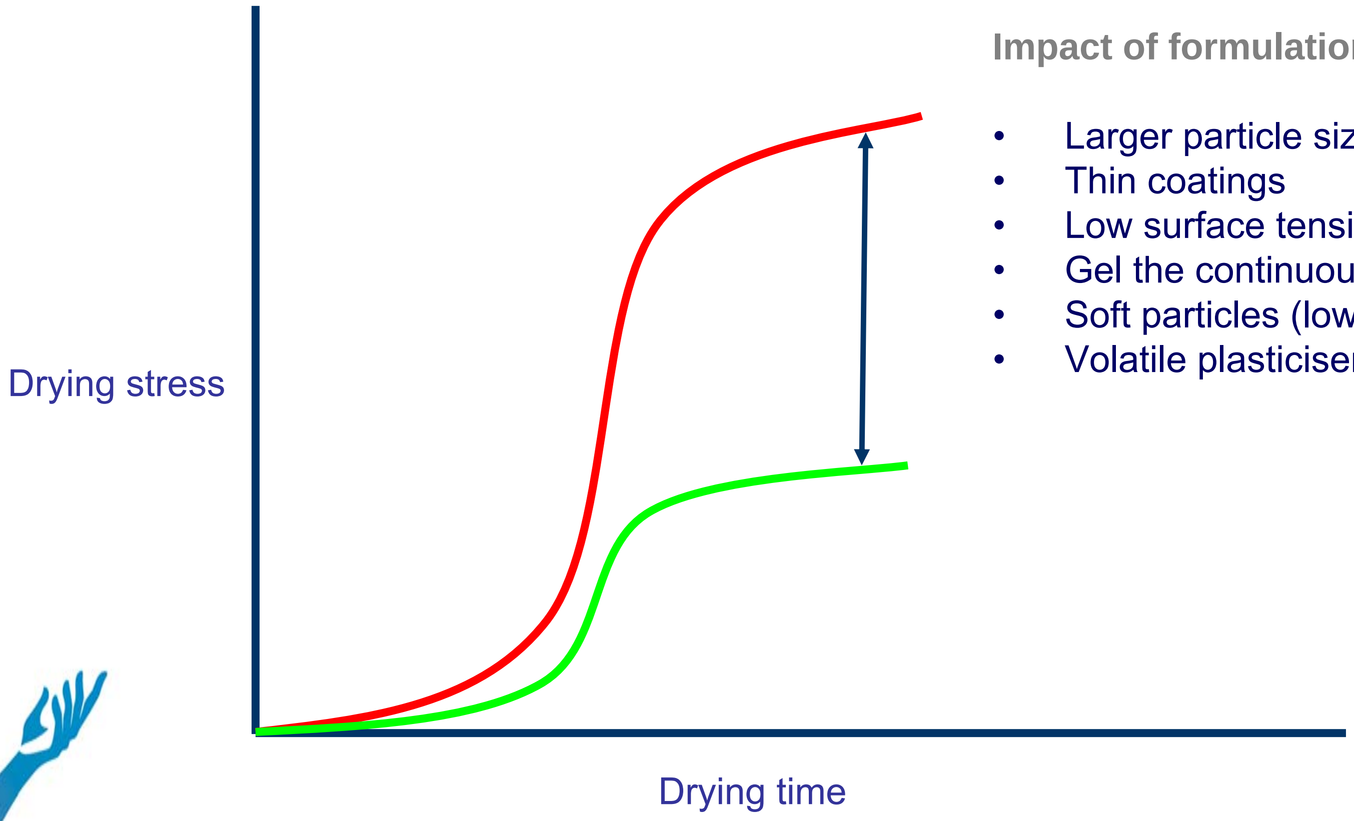


For many commercial materials the starting solids is such that stress begins to accumulate as soon as drying beings

From theory, we can now consider strategies to influence different parts of the drying stress profile

Managing the drying stress

Magnitude of the stress

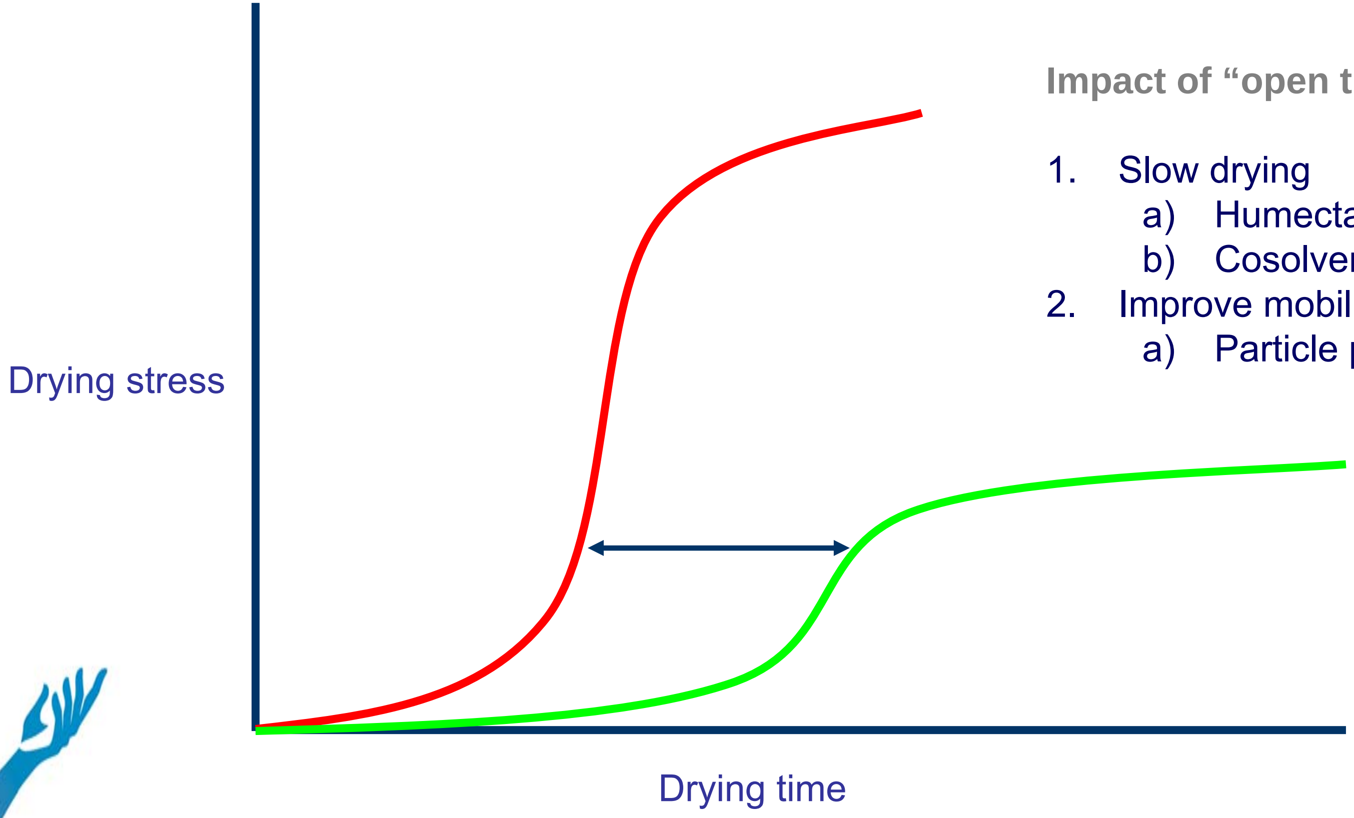


Impact of formulation components

- Larger particle size/lower SSA
- Thin coatings
- Low surface tension
- Gel the continuous phase
- Soft particles (low Tg)
- Volatile plasticisers

Managing the drying stress

Timing of the stress development

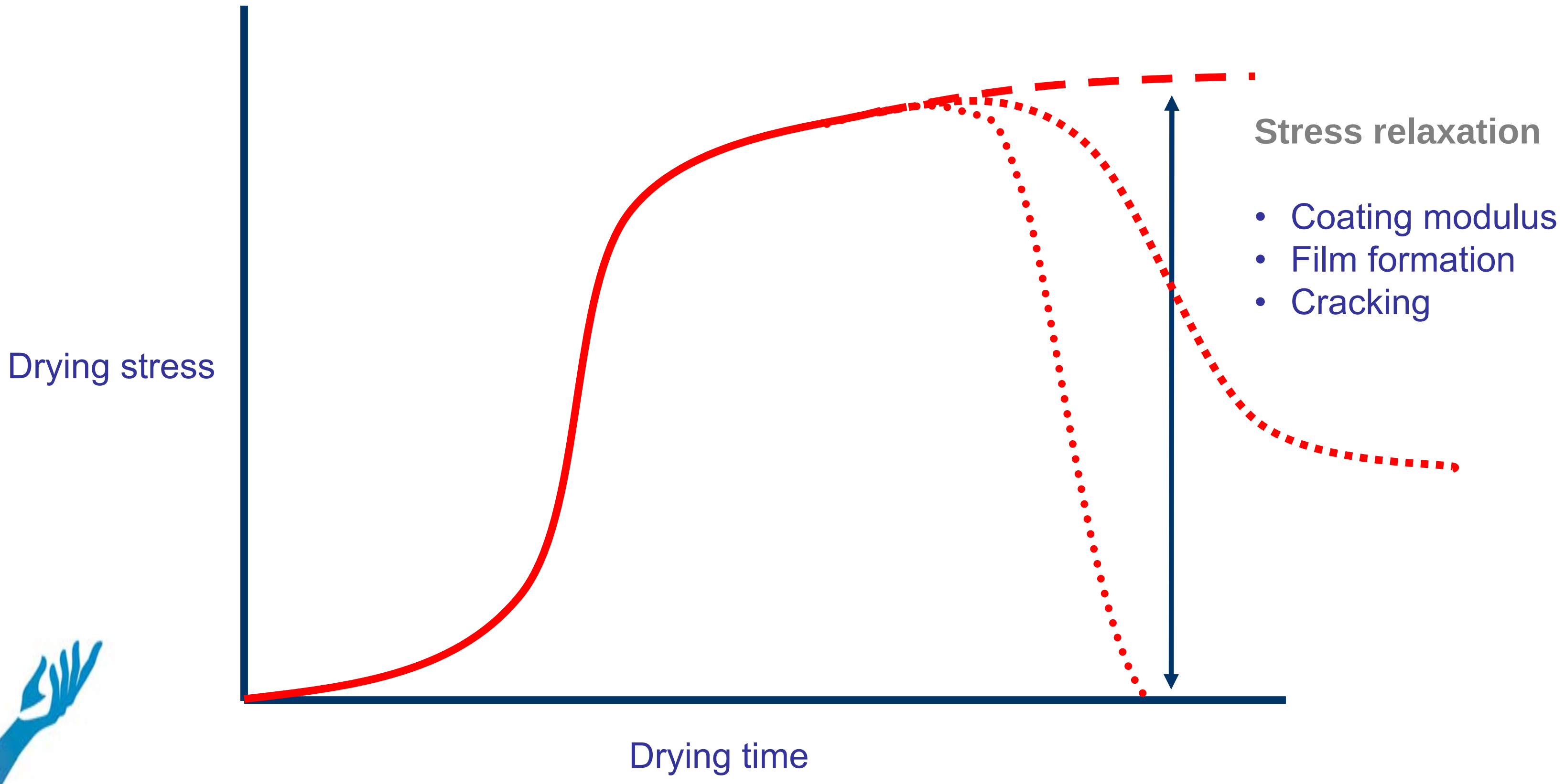


Impact of "open time"

1. Slow drying
   a) Humectants
   b) Cosolvents
2. Improve mobility vs. solids
   a) Particle packing

Managing the drying stress

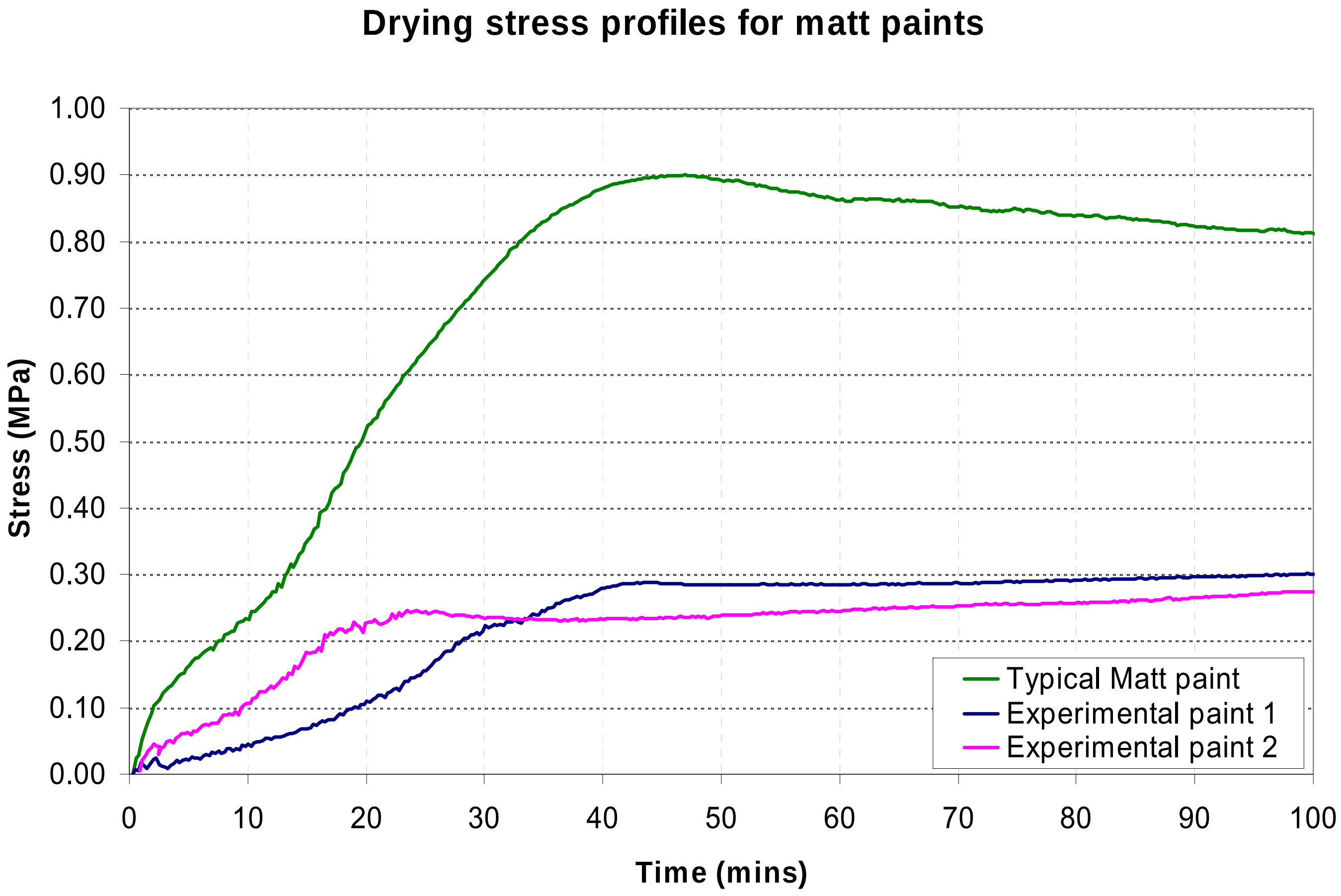
Retained stress



Stress relaxation

- Coating modulus
- Film formation
- Cracking

Managing the drying stress



Many paints possess a high level of “retained” stress after drying
However it is possible to manage this stress » improved service life

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Summary

- Drying stress generated by the capillary pressure during drying can be measured by cantilever bending tests
- These measurements, whilst not absolute, do provide insight into the dynamics of drying and stress rise
- Most, if not all, industrial/commercial materials are “high solids” materials and as such typically begin to develop drying stress immediately upon application
- Compressional rheology measurements can also provide insights into network consolidation and strength under drying/dewatering

Taking stock…..

- Particulate networks are put under compression during drying by capillary forces
- The capillary forces are balanced against the yield stress of the concentrating particle network
- Consolidation during drying strengthens the particle network
- If the yield stress of the network is greater than the maximum capillary pressure then liquid recedes into packed particle network
- Alternatively the coating cracks under the transverse stresses caused by shrinkage strain imposed by the pinning of the coating to the substrate

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Taking stock…..

- Theory suggests coating cracking should depend on;
  - Capillary pressure
    - Specific surface area, surface tension, volume fraction and contact angle
  - Coating thickness
  - Wetting of the substrate
  - Evaporation rate
  - Particle deformability (T_g) & shear modulus
- How well do these guidelines predict the behaviour of industrial systems?

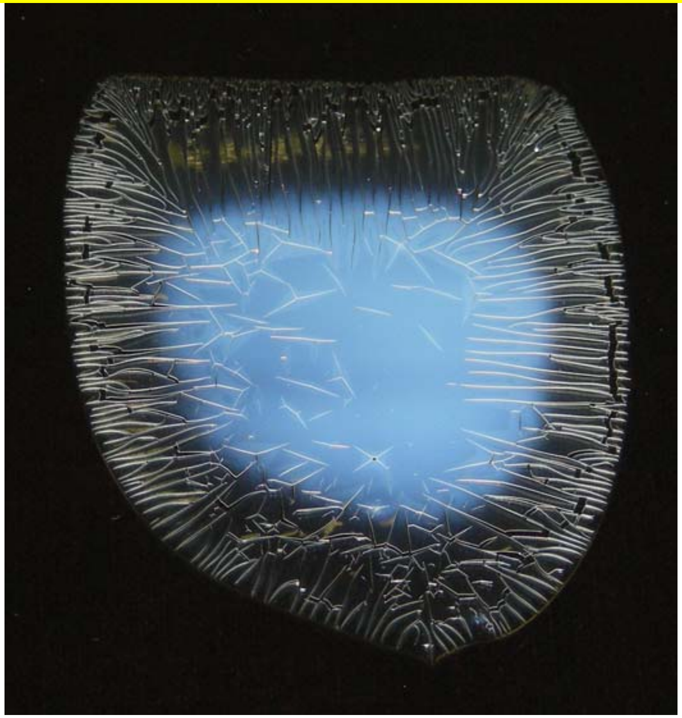
Influence of drying rate

Influence of drying rate

Latex with following properties

Particle size	200nm
Polymer T_g	17°C
MFFT	15°C
CCT*	10µm

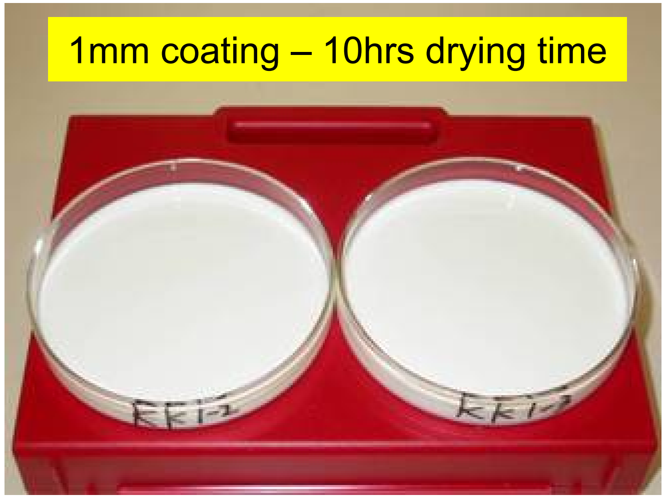
150µm coating – after 50mins drying time
Time for complete drying – 70mins



*20°C/50% RH

Influence of drying rate

Despite a CCT of only 10µm, it is possible to produce thick, crack free coatings – if you are willing to wait long enough


1mm coating – 10hrs drying time

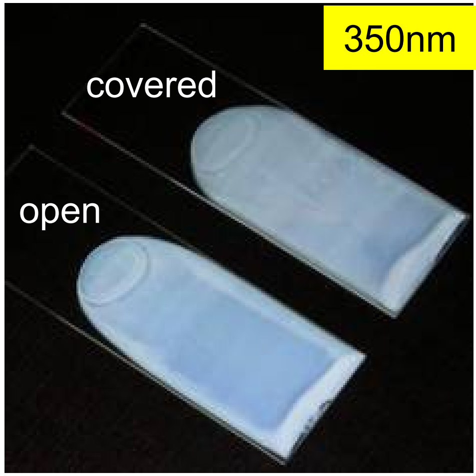

1mm coating – 35hrs drying time

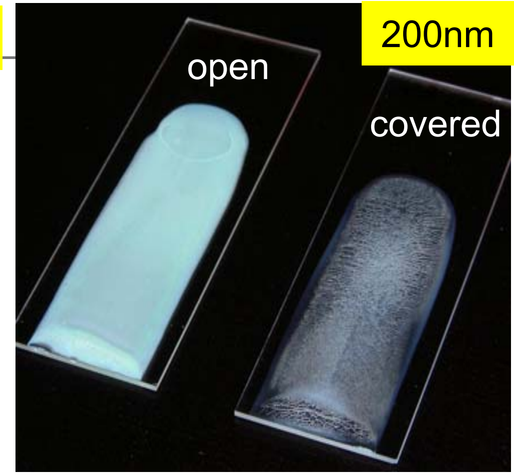
Faster drying results in increased propensities to cracking

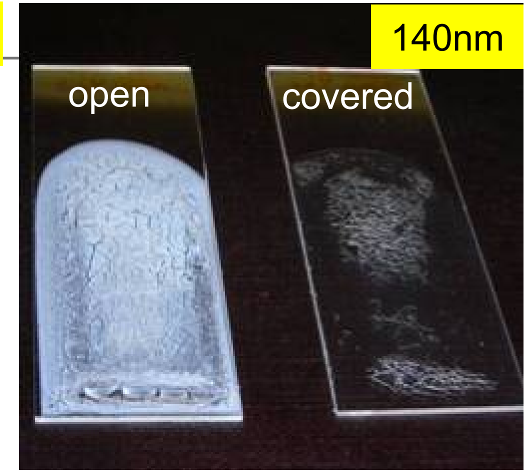
Slower drying influences network strength development during consolidation

e.g. Timeframe for visco-elastic response of latex particles

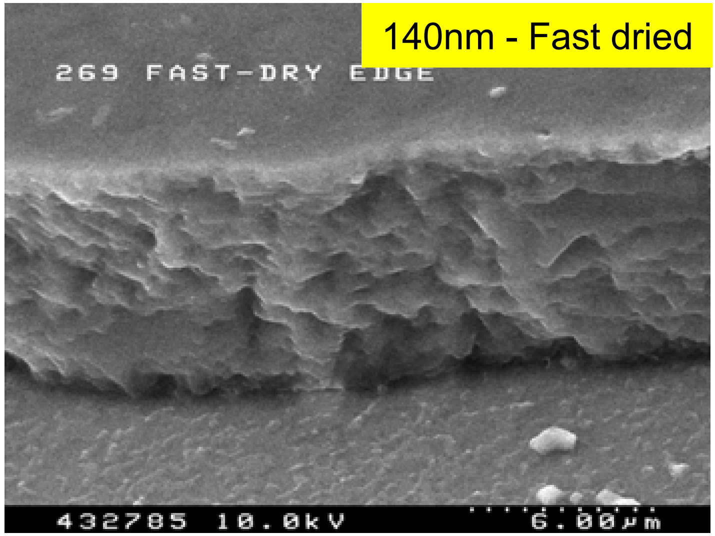
Influence of drying rate

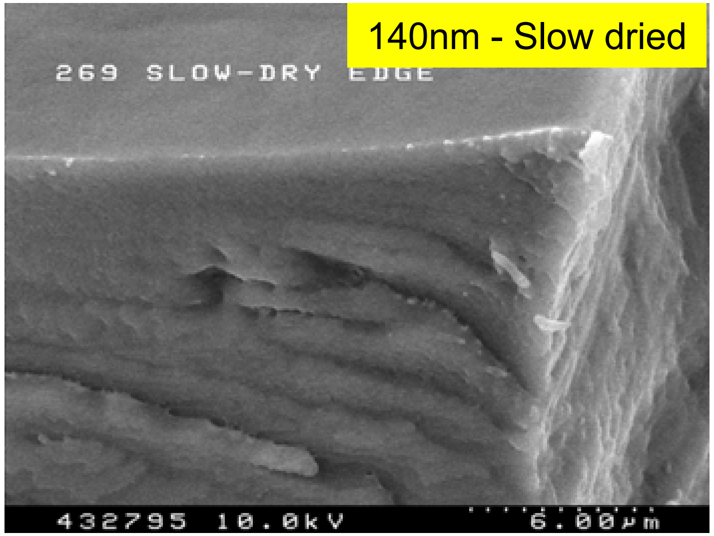






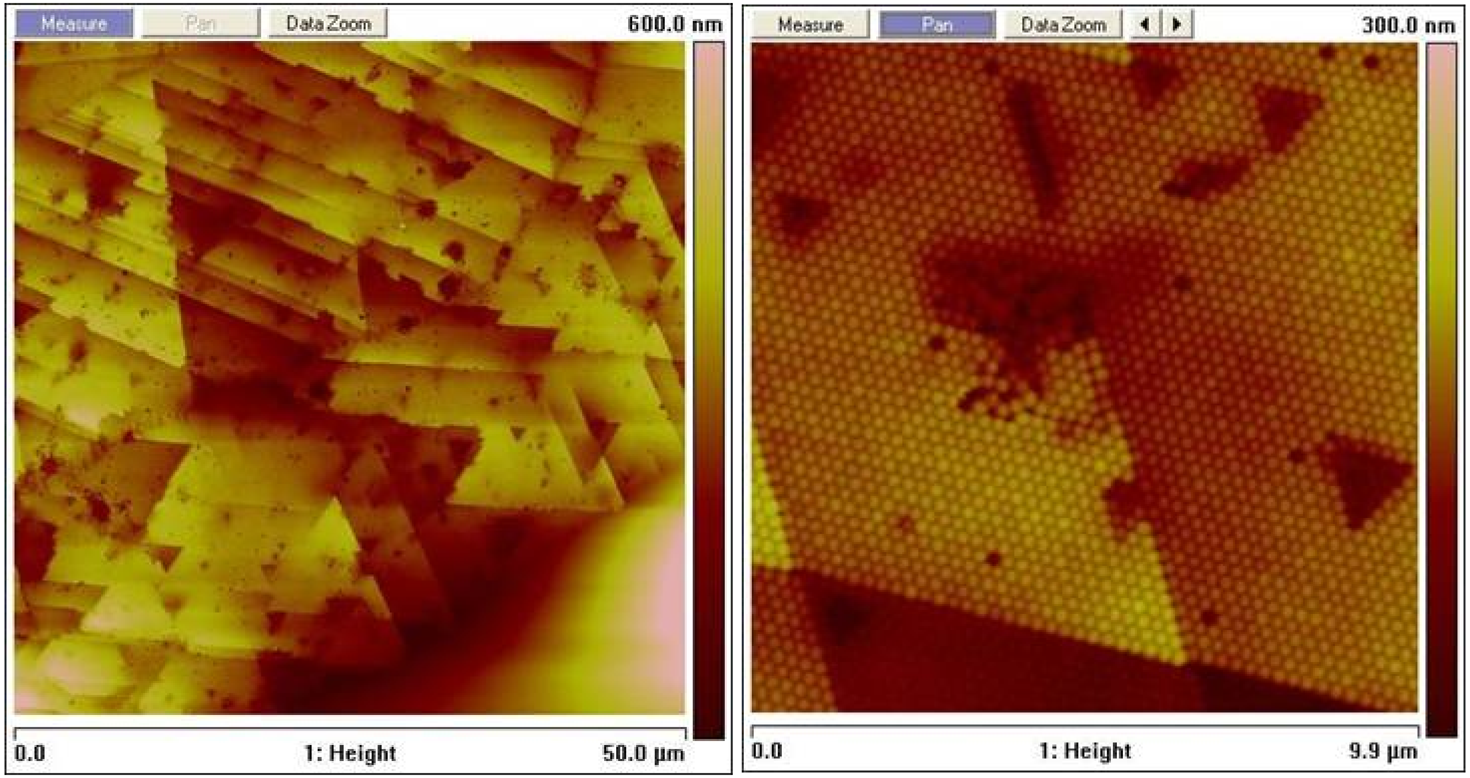
As latex particle size is reduced there is a greater influence of drying rate
SEM images reveal greater porosity in fast dried coatings





Influence of drying rate

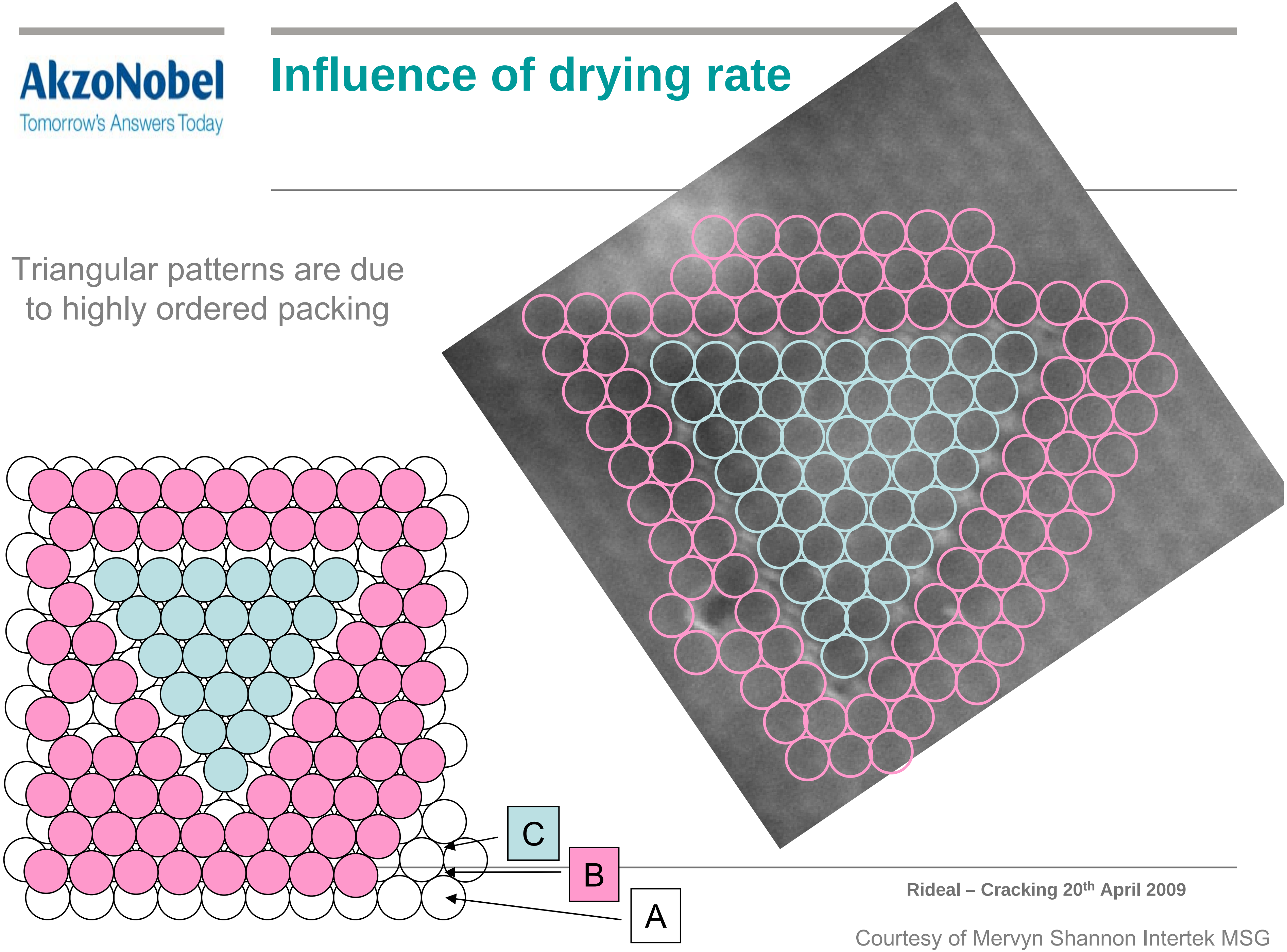
AFM images of the surface of slow dried coatings



Particle packing is highly ordered – unusual triangular symmetry
HCP interrupted with regions of random packing

Influence of drying rate

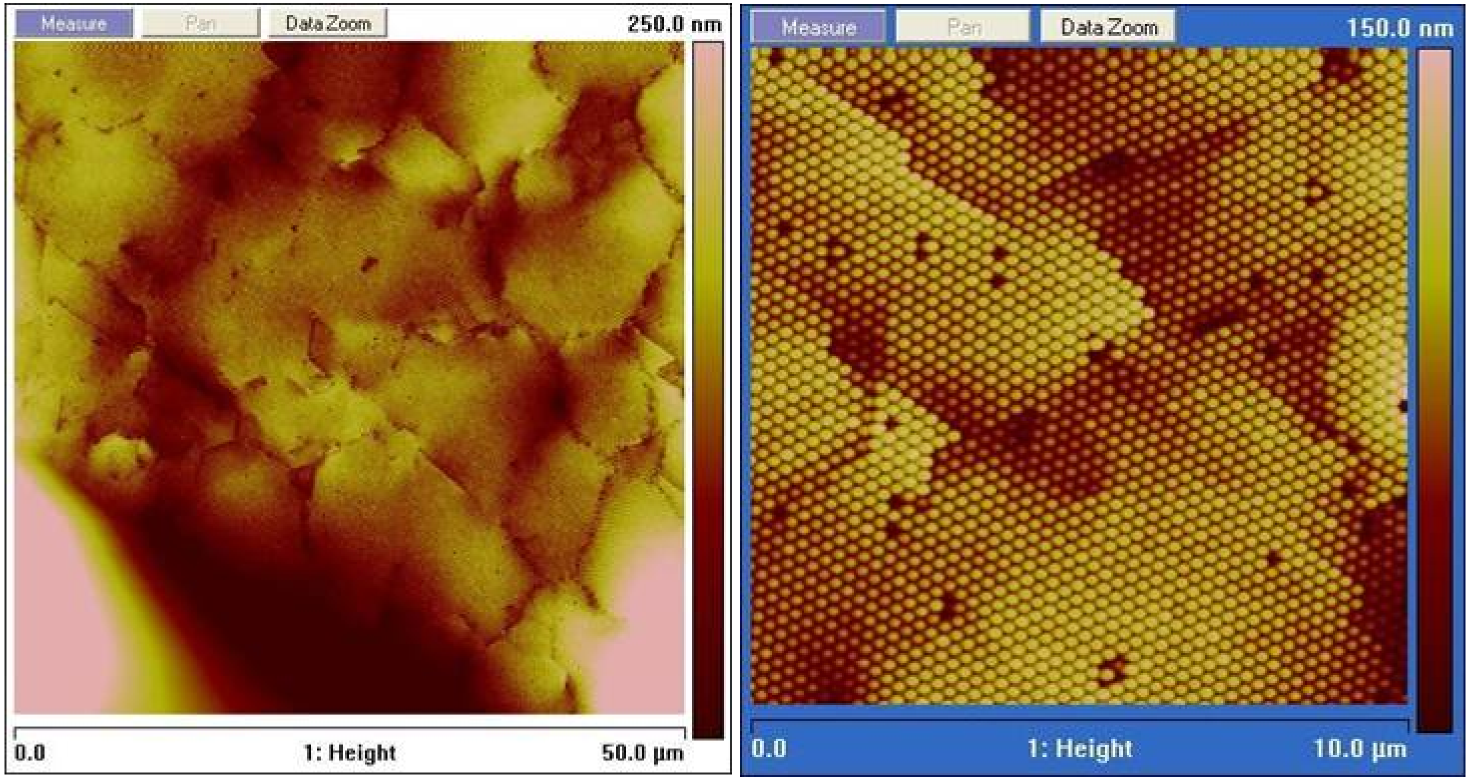
Triangular patterns are due to highly ordered packing



Courtesy of Mervyn Shannon Intertek MSG

Influence of drying rate

AFM images of the surface of fast dried coatings



Particle packing is still ordered – but less so than in the slow dry case
Grain boundaries/possible Bernard cell structure visible
Such small differences in the network order influence the CCT

Influence of specific surface area (SSA)

Influence of specific surface area

- The SSA influences the maximum attainable capillary pressure
- Particle size itself shows a poor correlation with the CCT
- Surface roughness/internal porosity contribute to the capillary pressure

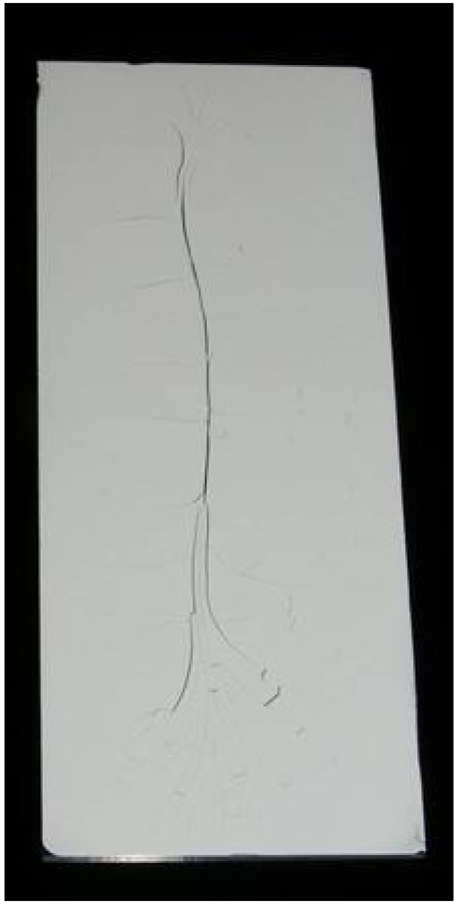
Measured particle size

- We have measured the CCT for a wide range of inorganic and organic particles

Styles of cracking for various inorganics

Colloid silica

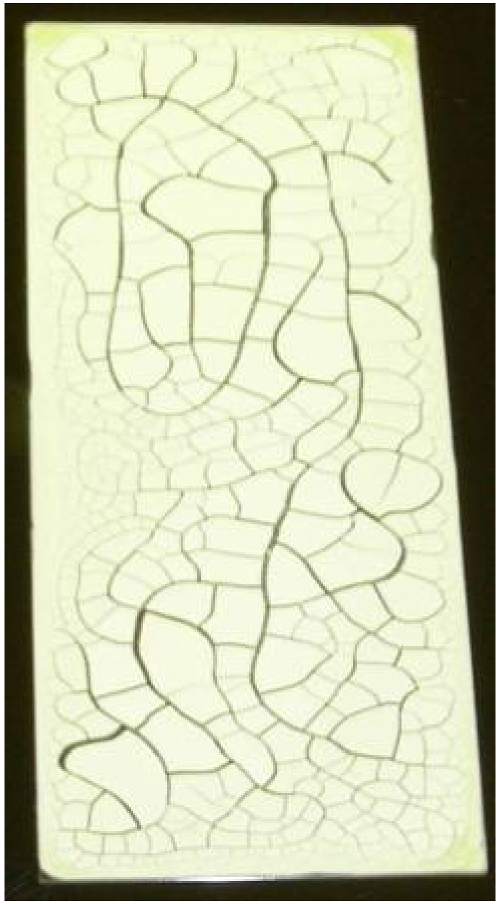
Titanium dioxide



Calcined kaolin

Styles of cracking for various inorganics

Indium tin oxide

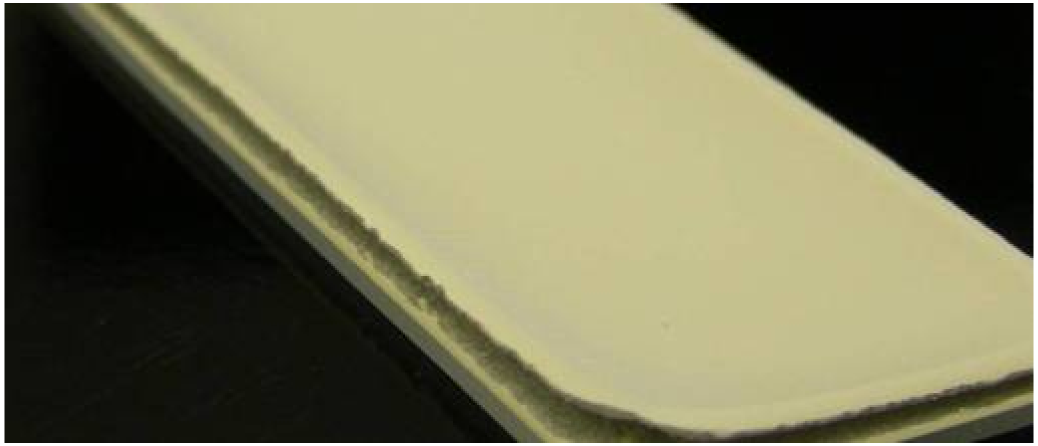


Mica

Yellow oxide

Styles of cracking for various inorganics

Kaolin



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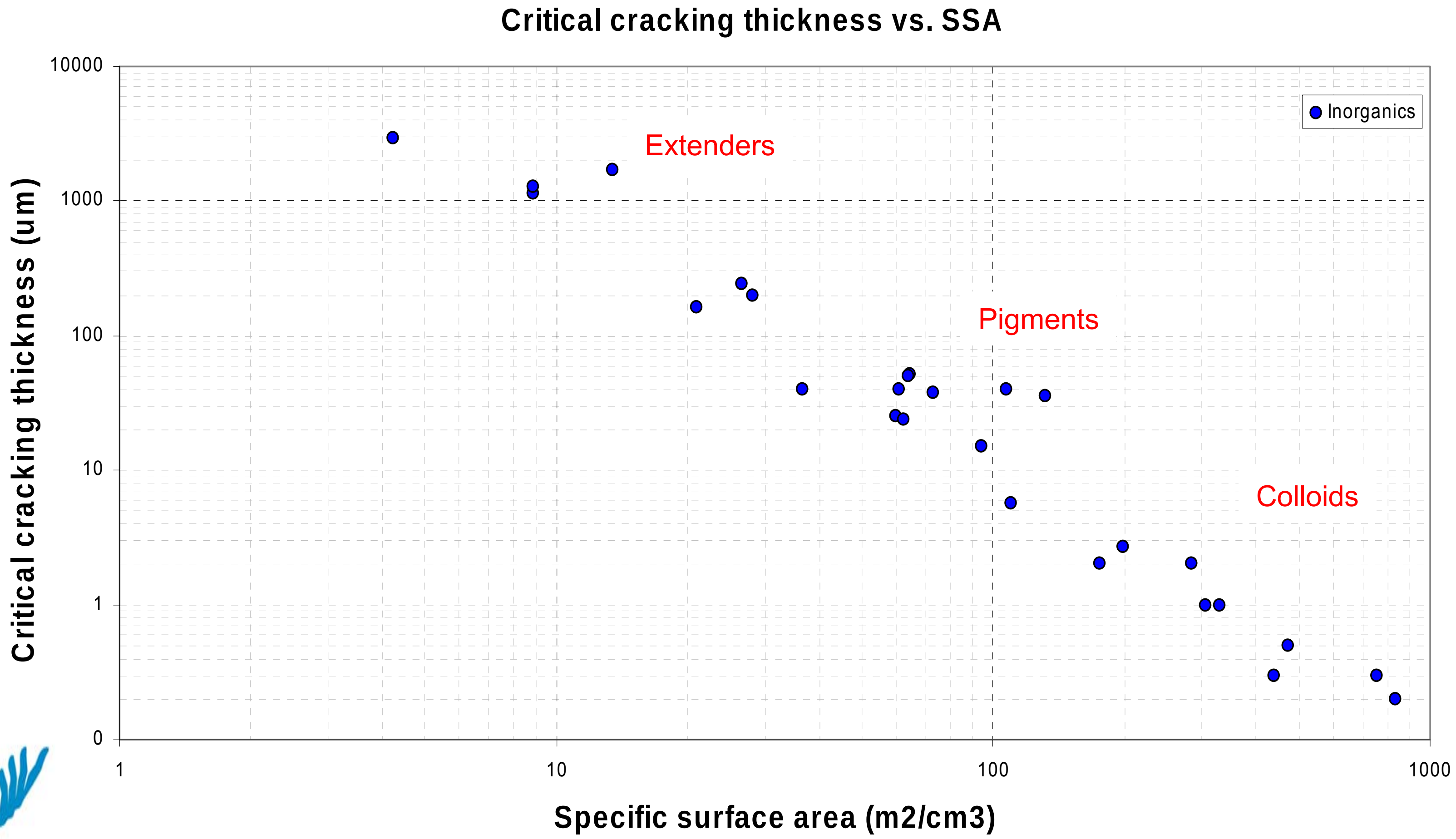
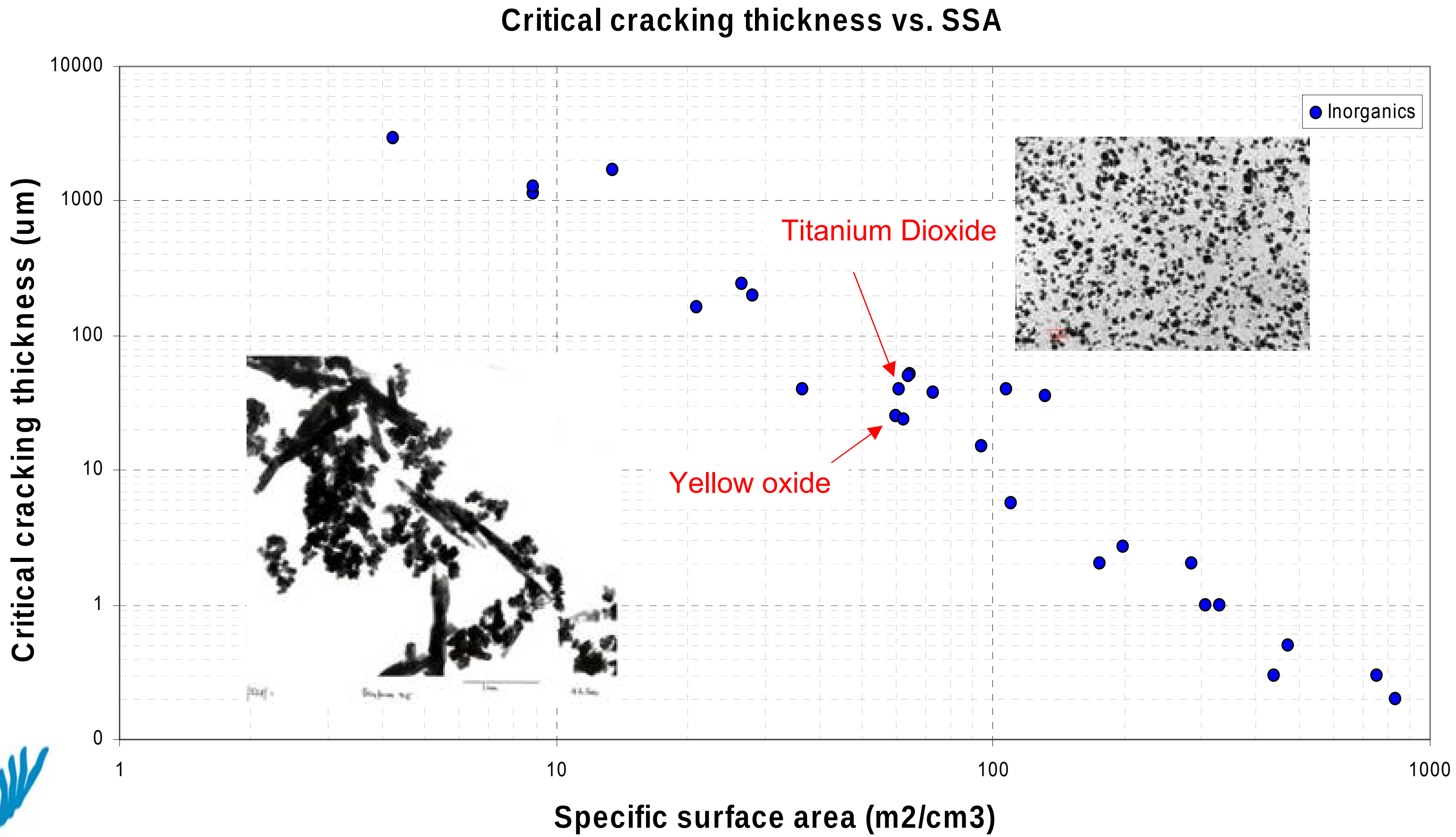
Influence of specific surface area



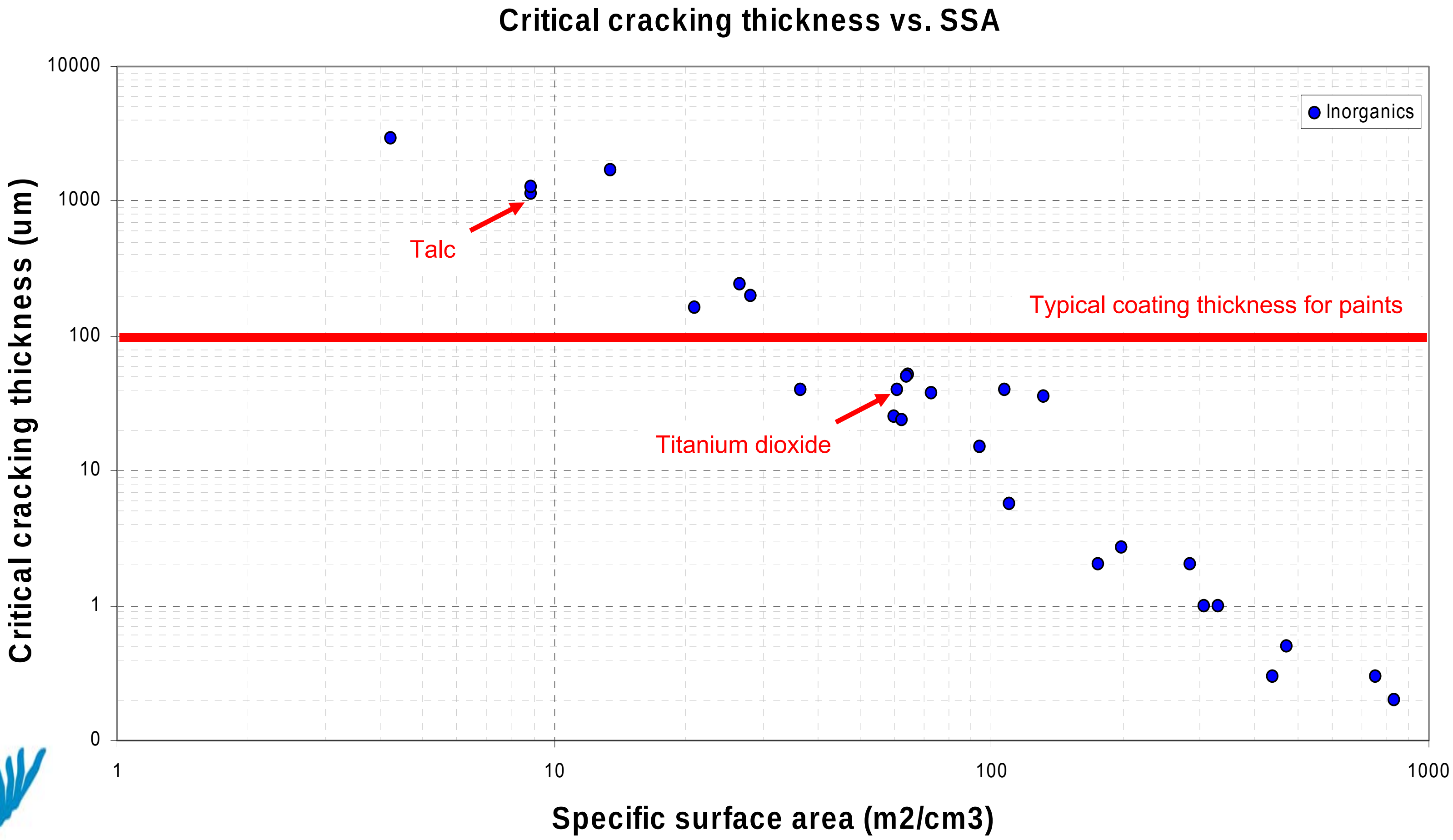
All of this data is based upon stable dispersions without added binder
Crack-free binderless coatings are possible – of limited use

Influence of specific surface area



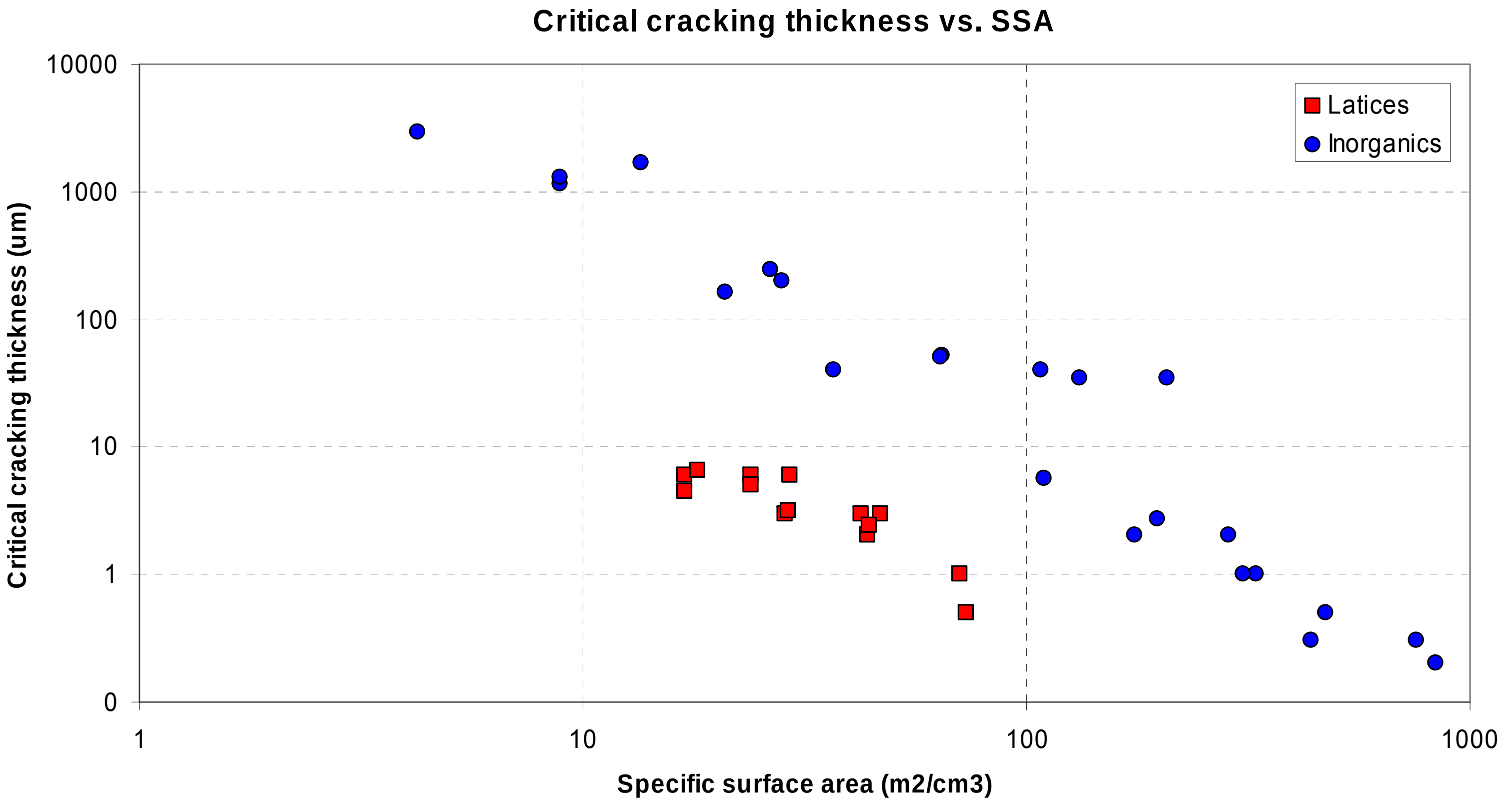
The SSA is the dominant factor – particle shape is a secondary influence

Influence of specific surface area



Many pigments have CCT’s below the typical thickness of decorative paints
Necessitates formulation with lower SSA extenders and film forming latices

Role of specific surface area



The role of SSA still holds true for latices
However we have a narrower experimental range available to us
Polymeric particles are more prone to cracking than the inorganic materials
This is due to the lower inherent modulus of the (non-film forming) polymerics

Summary

- Out of all the factors we have studied by far the greatest to influence cracking behaviour is the particle SSA
- For hard particles it has an over-riding effect on the CCT
- The CCT shows a remarkable correlation with SSA over a wide experimental space
- Other factors such as drying mechanism and particle shape are secondary
- This makes the SSA a valuable tool for formulators in industry
- Directs the choice of particle to maximise the CCT
- Useful if particle function isn't related to SSA

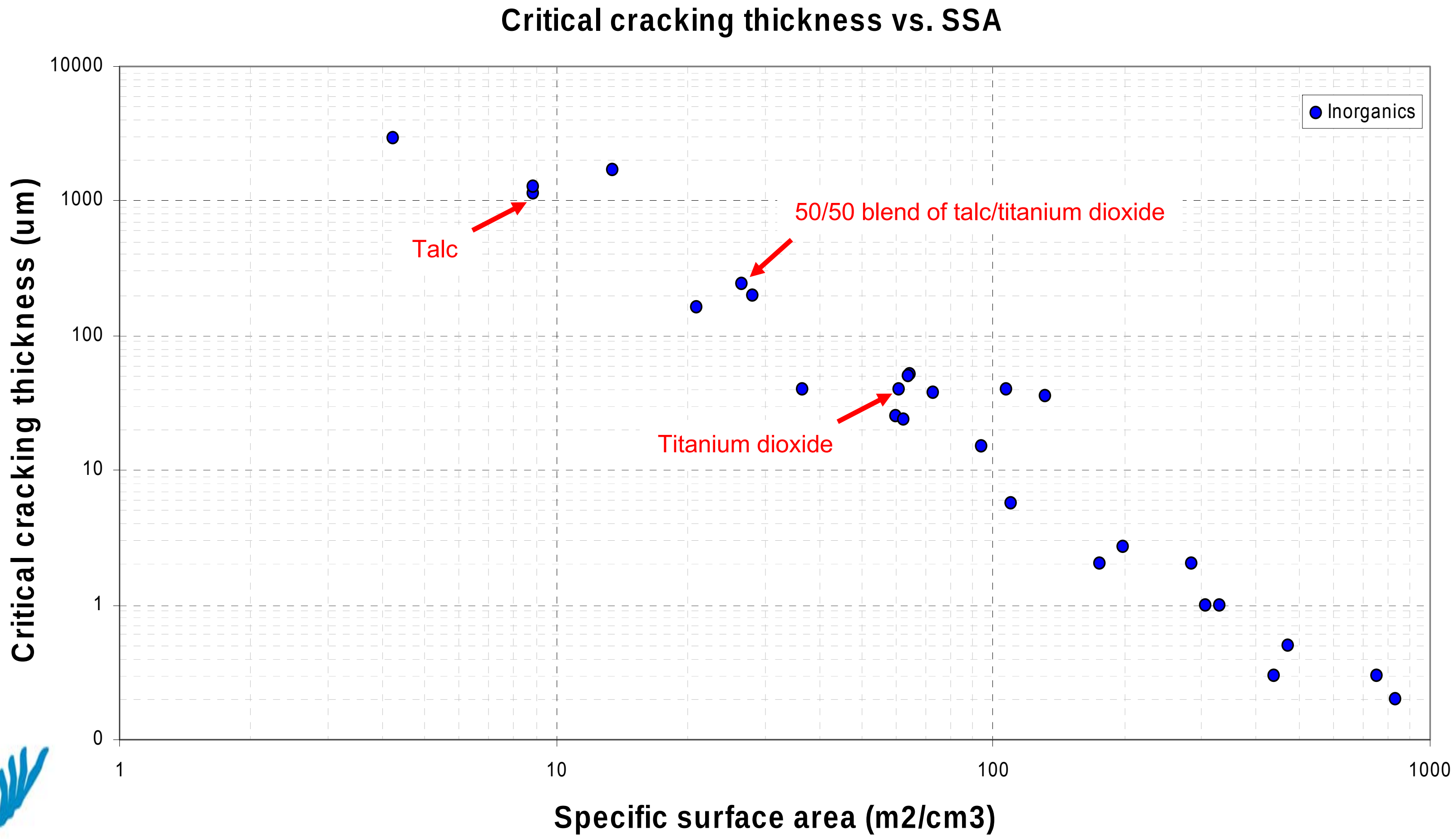
Particle blends

Particle blends

- What we have reviewed so for only covers model systems comprised of single particle types
- Obviously for industry this is far removed from reality
- Do the same formulating rules and guidelines apply when we start to blend particles?
- Does the capillary pressure generated by the smaller particles dominate the cracking behaviour?

- We have considered inorganic/inorganic particle blends and then hard/soft polymer latex blends

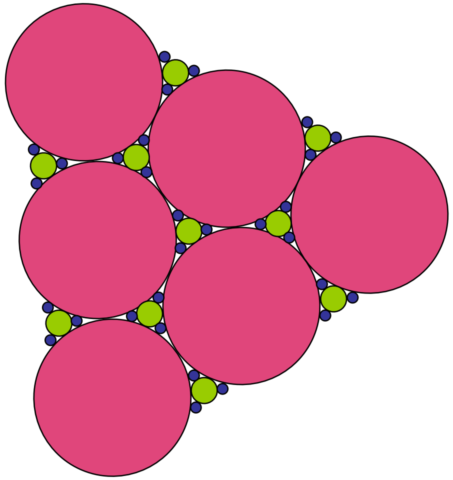
Particle blends



Generally blends of inorganic particles results in intermediate behaviour
The CCT can be predicted by averaging the SSA of individual particles
However in some cases particle segregation can cause one SSA to dominate

Particle blends

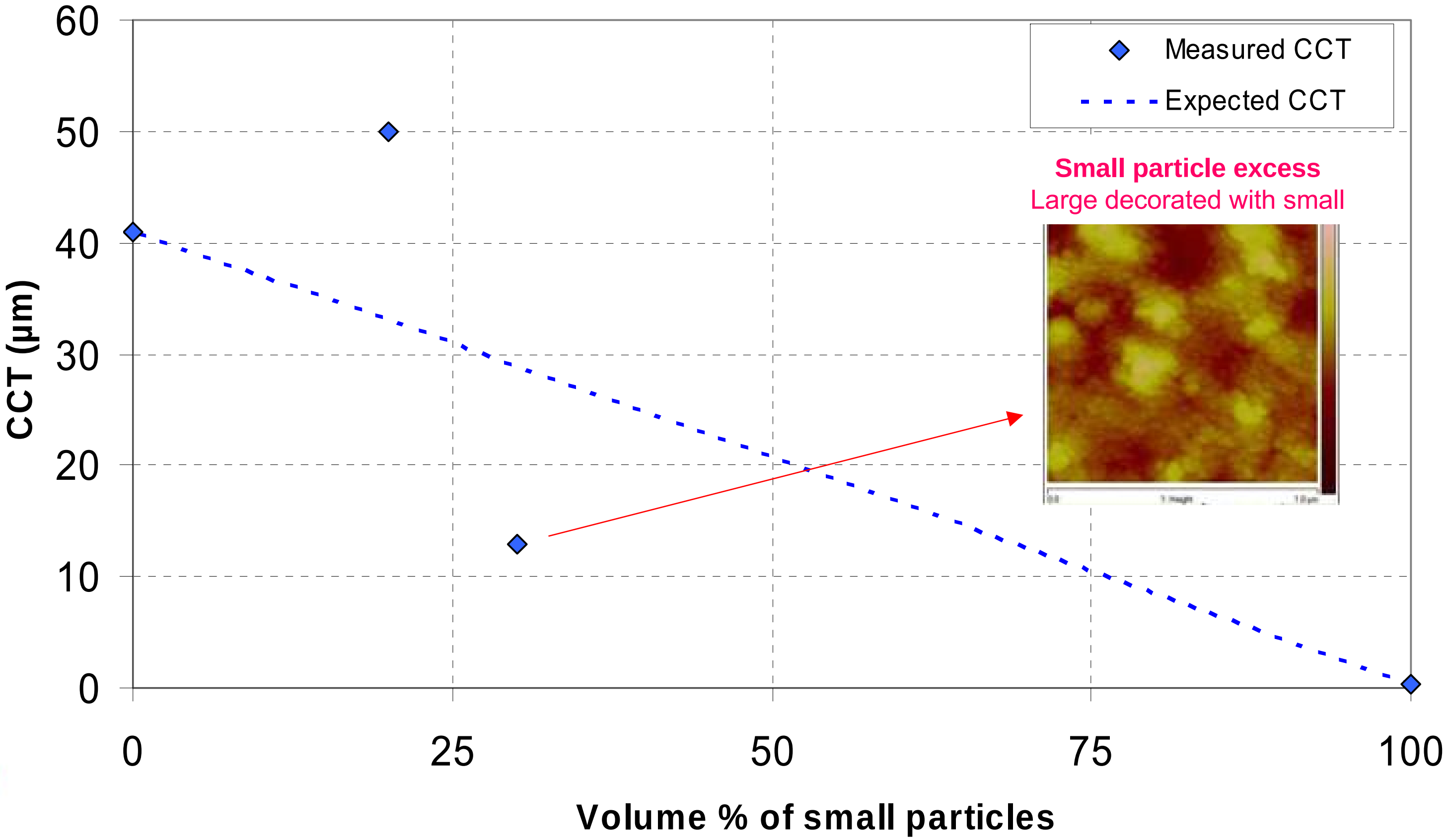
- Blends of greatly different particle sizes can lead to greater packing efficiencies
- E.g. the well known “Farris effect” can be used to reduce the viscosity of formulations at equivalent volume fraction
- The theory relies upon blending large/small with size ratios of >6:1 and in volume ratios of ~70:30



- 2nd, 3rd generational packing
- Increasing number of particle-particle contacts
- Increasing network “strength”
- Increased resistance to cracking

Particle blends

CCT of large & small particle blends (~20:1 size ratio)



Excess of small particles leads to lower than expected CCT
However there is a “sweet spot” with higher than expected CCT
This comes from efficient packing of the small/large particles

Hard/soft latex blends

- For latices the polymer T_g has an over-riding influence on crack behaviour
- As the coating temperature approaches the polymer T_g the CCT tends to infinity
- Below the T_g, the SSA of the latex dominates the CCT
- What happens if we blend soft latex with hard latex?
  - Mimic of filler inclusion in film forming latex
- How is the CCT affected?
- Latices with T_g's of 15°C and 60°C (same particle size of 128nm) blended in various ratios & CCT measured at 25°C

Hard/soft latex blends

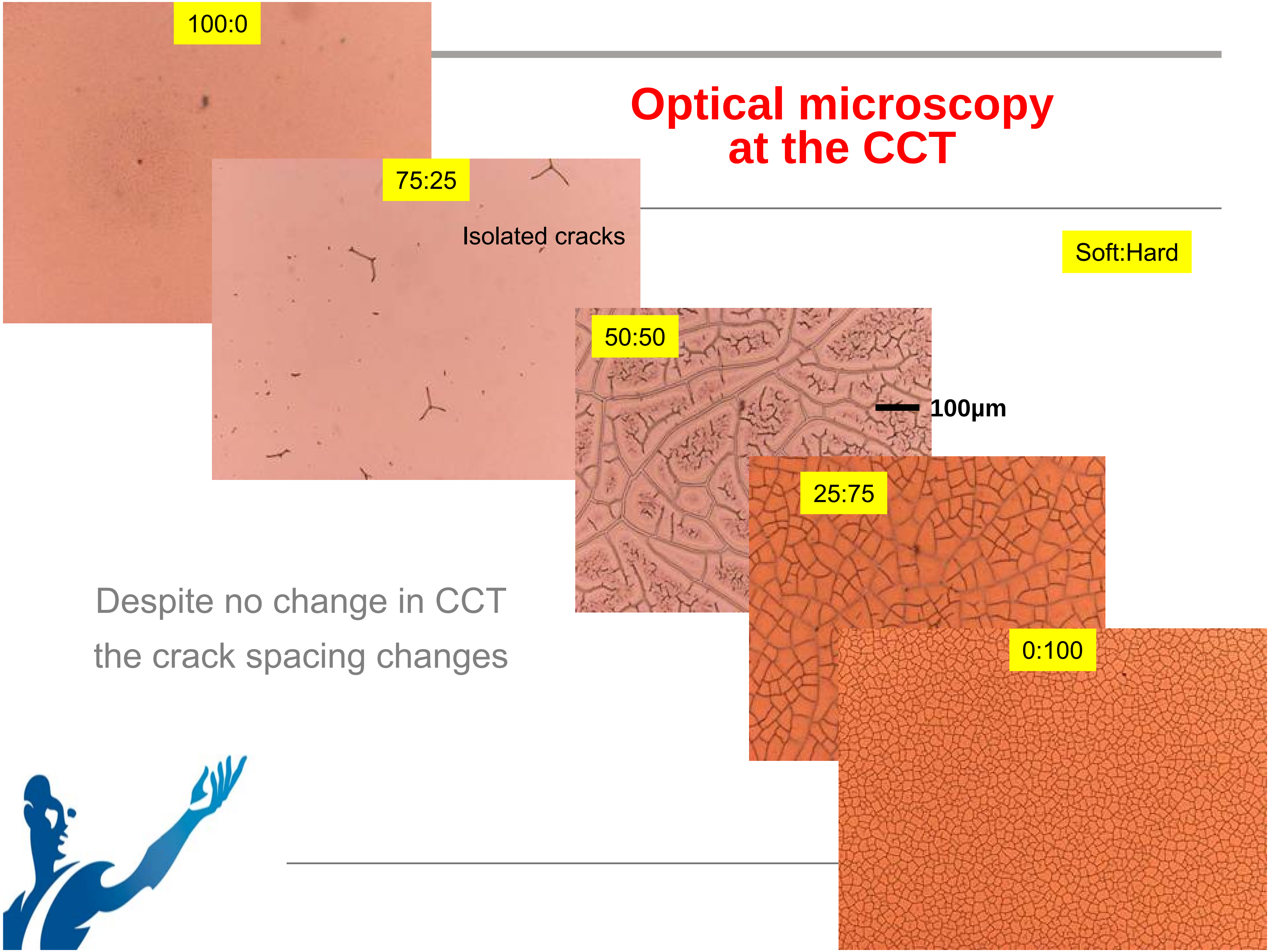
Blend (soft:hard)	CCT (μm)	T_g (°C measured/Fox)
100:0	None	15
75:25	None	25
50:50	6	35
25:75	6	45
0:100	6	60

When coated at 25°C the soft latex doesn’t exhibit any cracking

Cracking only occurs when the level of hard latex reaches 50wt%

There is no correlation of CCT with predicted T_g for the blends

Optical microscopy at the CCT



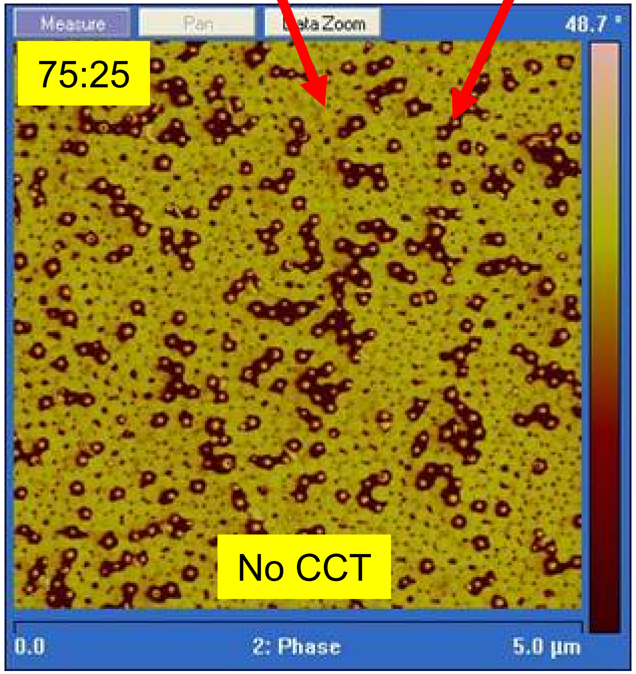
Despite no change in CCT
the crack spacing changes

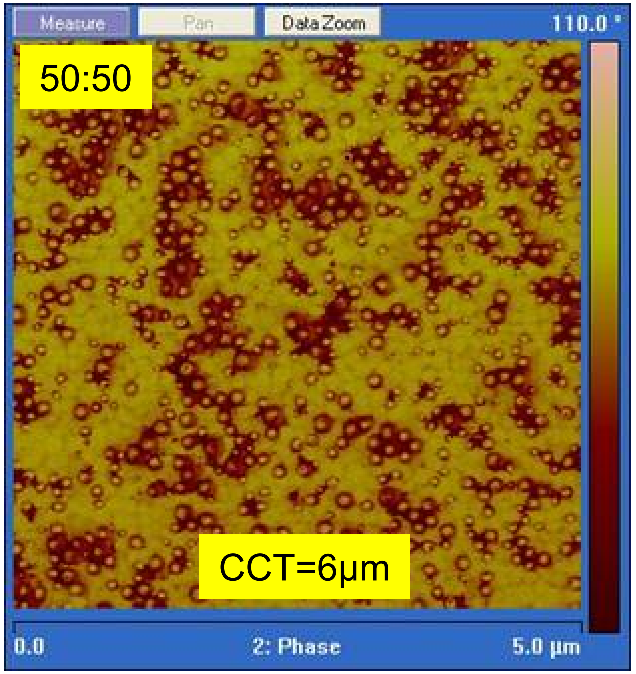
Hard/soft latex blends

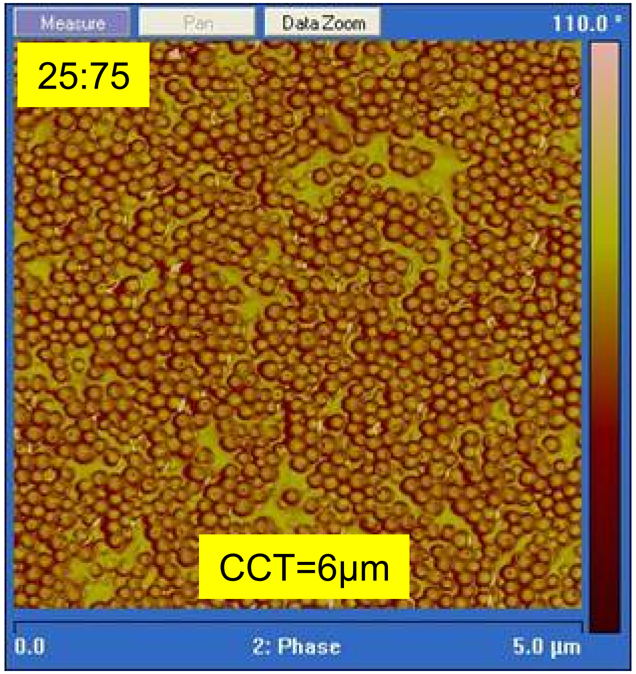
Soft latex

Hard latex

Soft:Hard







Once the hard phase percolates a CCT is observed

Summary

- Systems consisting of more than one particle can exhibit a range of cracking behaviours
- In the simplest case the CCT can be predicted by the averaged SSA of the individual components
- However it is often the case that particle segregation, stratification and percolation thresholds influence the cracking behaviour making it more difficult to predict
- Prediction in such systems relies on an understanding of the final film morphology and any heterogeneities

Conclusions

Where have we got to?

- Current trends in legislation and private & public sentiment are driving formulators down paths that lead to cracking
- Industry has to address these needs without compromising other coating properties and profitability

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30% Lower
Carbon Footprint*

step towards **greener**

*As compared to Dulux Matt 2008 formulation,
to find out how we have calculated the reductions,
visit www.dulux.co.uk/enviroment.

Where have we got to?

- Significant advances have been made in the last decade regarding the factors that control and influence the cracking upon drying of colloidal dispersions
- It is the capillary pressure generated during the drying of particulate dispersions that is responsible for the stresses that cause cracking
- The over-riding contribution to the capillary pressure is the specific surface area of the particles
- The simplest handle a formulator has control over when facing a mud-cracking problem is the SSA of the component particles

Where have we got to?

- A critical coating thickness exists for colloidal coatings – this represents a transition point between crack-free and cracked coatings
- The CCT correlates with the SSA over a wide experimental space, particularly for inorganic particles
- The mechanism of drying and cracking does not seem to influence this correlation
- A robust predictive model exists to describe the CCT of both inorganic and polymeric hard particles

Where have we got to?

- Polymer latex particles only exhibit cracking during drying if the polymer T_g is higher than the coating temperature
- Film forming latices do not crack – the drying stress is relaxed by the deformation of the polymer particles
- The shear modulus of the particles influences the CCT, such that polymer particles are more sensitive to cracking than hard inorganic particles
- The drying rate does have a role to play in defining the cracking behaviour, particularly for polymer latices, however commercial exploitation of this effect is limited

Where have we got to?

- Blending of particles introduces further complexities
- For many hard particle mixtures the CCT can be predicted from the average SSA of the particle mix
- For hard/soft particle mixtures, it is the percolating phase that defines the CCT behaviour, although the crack spacing may change irrespective of the CCT
- However in both cases segregation of the particles, or structuring of the particles can have either a positive or negative effect on the CCT
- Controlling the film morphology to control the cracking behaviour is an area that offers potential

What remains to be done?

- Our understanding of blends and mixtures is beginning to grow but there is a lot of ground to cover
- In particular we currently have a limited understanding of the critical factors when hard particles are blended with a binder
- The binder introduces a number of other variables;
  - E.g. Overall modulus of the coating, drying kinetics
  - Viscosity vs. solids profile, coating morphology
  - Mechanism of drying stress relaxation
- The interplay of these factors means that the role of the binder is not simple but also means that there are several handles we can turn

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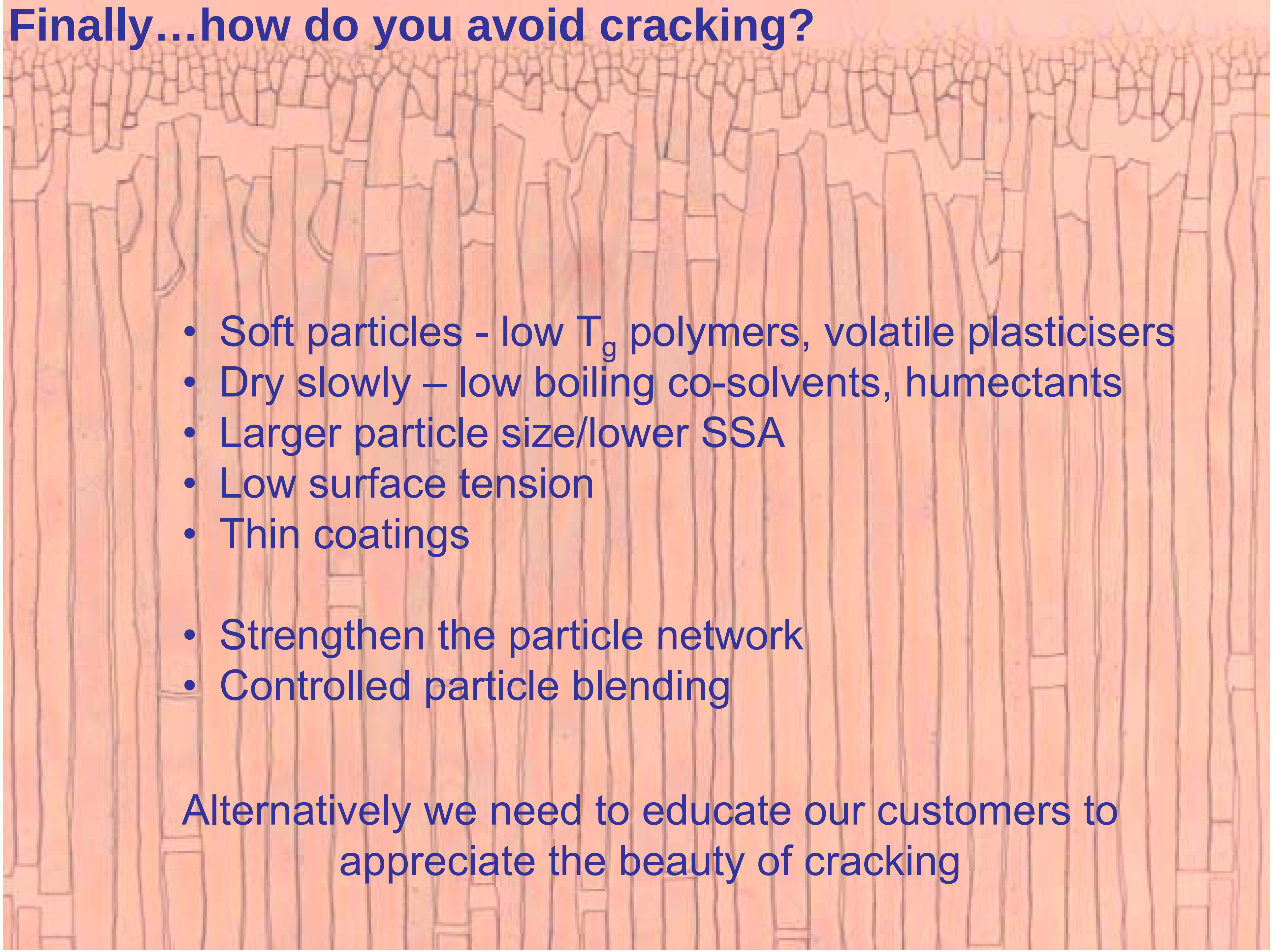
What remains to be done?

- Most - but not all - of the work in this field has been concerned with stable dispersions
- Flocculation changes the co-ordination number, final volume fraction and network strength
- Thus we would expect flocculation to have a significant influence on the cracking behaviour
- Tirumkudulu et al. have shown that the CCT of flocculated systems can be predicted using the current models
- This learning needs to be assimilated by industry

Finally…how do you avoid cracking?



- Soft particles - low T_g polymers, volatile plasticisers
- Dry slowly – low boiling co-solvents, humectants
- Larger particle size/lower SSA
- Low surface tension
- Thin coatings

- Strengthen the particle network
- Controlled particle blending

Alternatively we need to educate our customers to appreciate the beauty of cracking