Nanoparticles for coatings. Why is reality so much less than the promise?

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Background to the problem

- MacDermid Autotype make high quality coated films for the European, US and Asian market
- A typical single product is 1m m^2/pa of a 3-layer coated PET film with a 5µm UV crosslinked hardcoat surface
- Typical applications – touch screens, touch panels, appliance panels …
- Hardcoat must combine multiple (sometimes conflicting) functionalities – toughness, hardness, flexibility, anti-microbial, anti-static, anti-smudge …
- All key competitors are going to nanoparticle formulations
- Assume 20% by weight of nanoparticle. 1m m^2 = 5000kg of coating and therefore 1000kg of nanoparticles
- Not a huge quantity, but not small either
- Potential for mutually beneficial business

Our part of the business

A large, clean-room coating machine.

That's what we do well. We are not, and will not be nanoparticle experts

So good relations with nanoparticle suppliers are vital

No shortage of nanoparticles

- There is no shortage of companies who claim to have great nanoparticles
- There is no shortage of ways to make nanoparticles
  - Flames
  - Plasmas
  - Precipitates
  - Sol gel
  - Microemulsions
  - ….
- There is no shortage of offers of nanoparticles to provide almost anything one wants – hardness, scratch resistance, anti-static, anti-microbial, anti-smudge …
- Nanoparticles really hold great promise for the future
- But!

I don’t want to handle a nanoparticle

- For two reasons
- I’ve told our workforce that we will not be bringing new (dry) nanoparticles onto site, so they don’t have to worry about unknown health risks.
  - This was our response to the UK Royal Society’s report on health issues. Dispersed nanoparticles can be assumed to be pretty much safe, dry nanoparticles raise issues beyond our expertise to handle.
  - Nanosafety is a really big, complex issue
  - Therefore there are many “nanosafe” initiatives, but lots of confusion and little apparent progress
- I have no idea how to disperse nanoparticles and I don’t have the time, money, energy, expertise to learn

Dispersing is easy … and hard

- Of course it’s not all that hard to throw in a dispersing agent, throw in some dispersing energy, and hope for the best
- But here’s a cautionary tale
- Our excellent partner/supplier had developed an excellent silica nanoparticle dispersion in our favourite acrylate
- We worked with their dispersion and formulated to get great technical results.
- We, and our partner, started to scale up. Still no problems
- Then one new batch arrived that started to gel spontaneously
- And we found that when we scaled up to production-scale filters (to filter out general junk, not nanoparticles!) even good batches gelled instantly in the filters

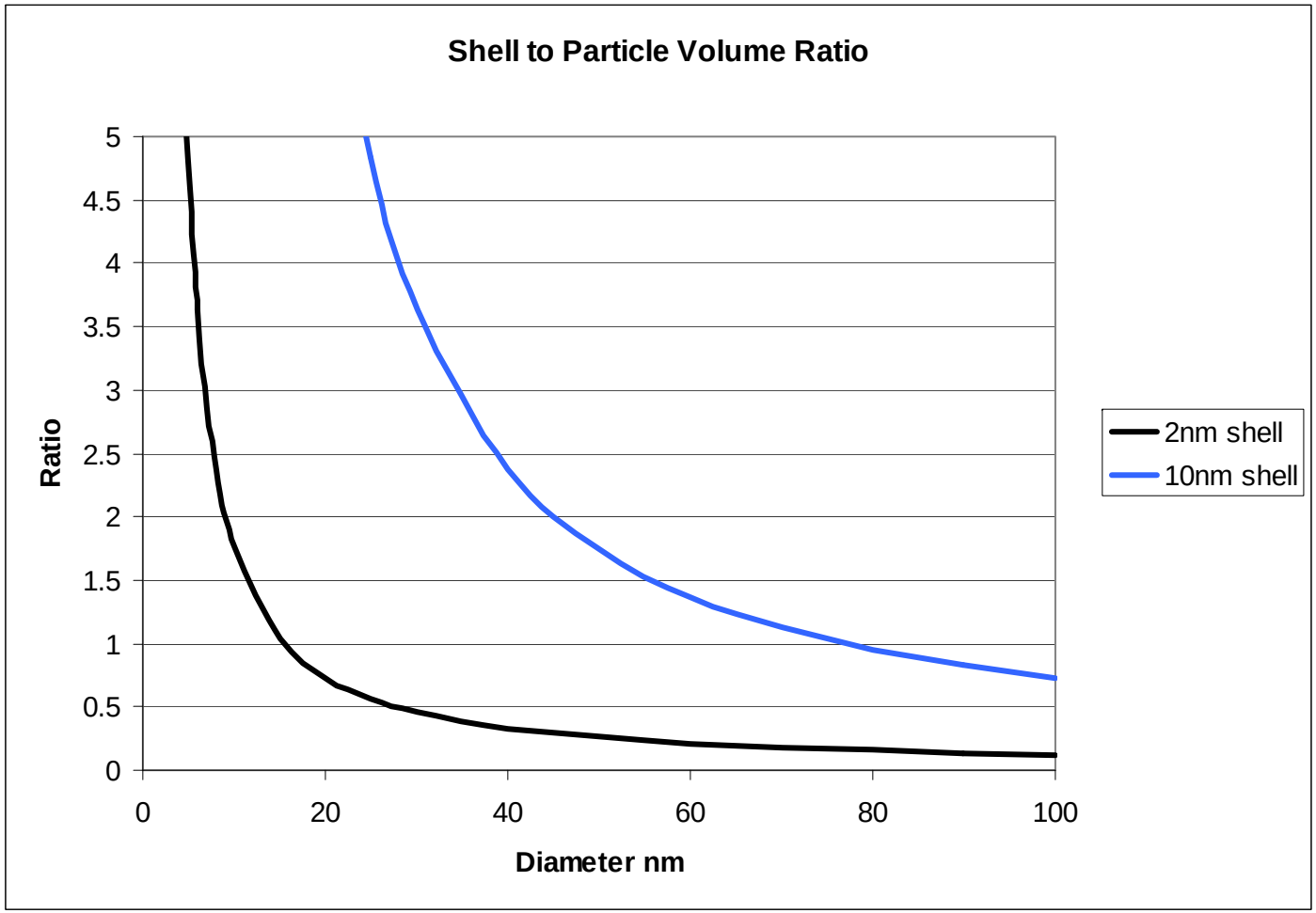
One year later

- It took our partner and ourselves one year of hard work to get over the problems
- This is one year of wasted commercial opportunity for both of us
- This was not due to stupidity or lack of hard work
- It’s simply a tough problem at the bleeding edge of nanoparticles
- Happily, the business is growing for both of us

- But this was for simple silica
- Imagine what it’s like for more exotic nanoparticles

- And then there’s another big problem …

… What is 25nm silica?



When we buy a "25nm" silica particle, if it is stabilised by a 10nm shell of polymeric disperser then there is 5x more volume of disperser than of silica

If I need nanoparticle properties then I want the thinnest possible stabilising shell. A 2nm shell on the same 25nm particle is half the volume of the silica

Small *is* beautiful

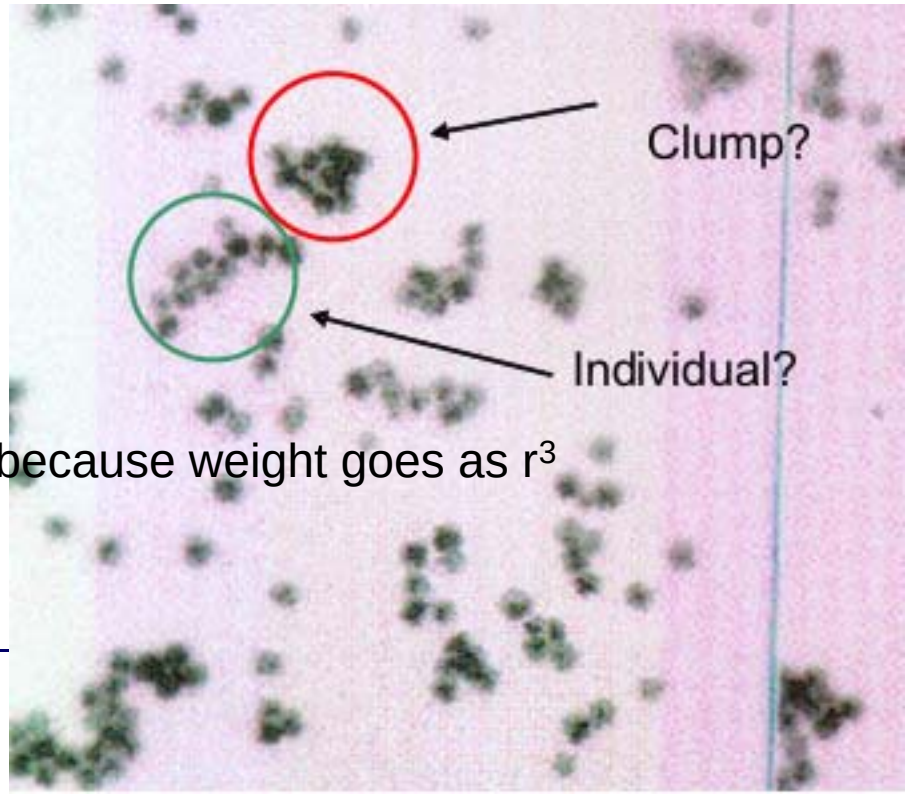
- Given that for most of us, smaller is better, the “shell” issue is critical
- I need smallness (especially with high RI functional particles) because my films have to be super-clear
- But I also want lots of surface area of my nanoparticle to deliver its properties to my matrix

- And I also want it to be locked in to my matrix, so I need the shell to be reactive with my matrix
- And I also want to know what’s really happening in my matrix but I don’t have the analytical facilities so I need my suppliers to tell me.

- It’s not that I’m greedy. These are basic requirements for most real-world applications.

What size are my particles?

- If you have 2 particles touching in a micrograph are they 2 small particles or 1 big particle?
- Manufacturers prefer the “small” interpretation
- Or they find a better picture
- Most quoted sizes are false
- Number % - small is favoured
- Weight % - big is favoured
  - 1 1µm particle = 10^6 10nm particles because weight goes as r^3



In this example they really were individual particles

Nanoclays

- Cheap!
- Easy!
- Dramatic improvements in properties!

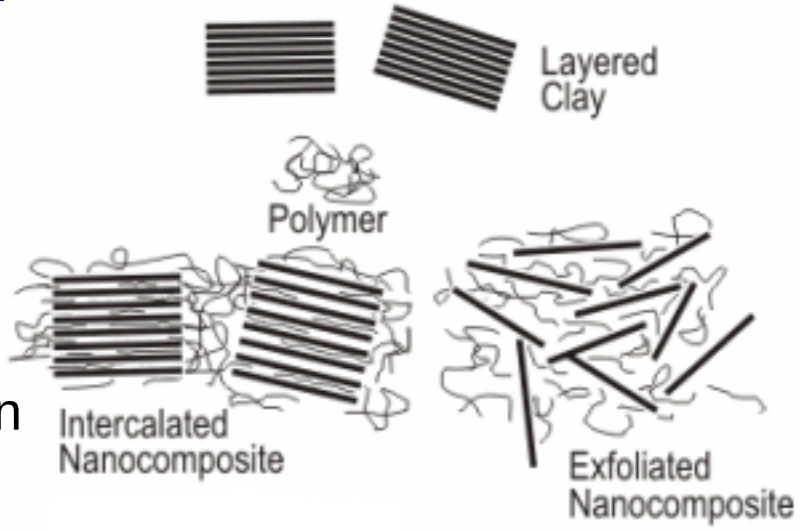


Image from www.azom.com

- But, in general, not for your application
- Not the fault of the organo-clay suppliers
- It's tough to exfoliate
  - You have to chose the right quaternary ammonium salt
    - The rules for polymer compatibility are poorly understood
  - You have to do the ion-exchange perfectly
- Cheap isn't compatible with 100% quality
  - I've looked at lots of academic papers which don't make much sense, probably because the clays weren't pure enough to start with

Carbon nanotubes

- Miracle wonder cure for everything!
- Will be available in multi-ton quantities real soon now!

- Except…
- They just love to self-clump
- Functionalising them for better dispersion is tough and even more expensive
- The big variety of “nanotubes” means a big uncertainty about optimum compatibility with dispersants, coating media

This isn't just *our* problem

- Essentially every other (potential) user of nanoparticles is going through the same painful learning curve
- This hurts the users and the suppliers
- If we all do it independently then the take-off of nanoparticle business opportunities will be painfully slow

Creating a real nanoparticle business

- Particle suppliers would love simply to ship tons of dry powders
- Dispersion experts would like to sell dispersing machines and chemicals
- End-users want to buy in a particle of their choice dispersed in a medium of their choice with guarantees of small particle size, small shell, infinite dispersion life, robustness to failure during subsequent processes
- Analytical equipment providers want to sell expensive machines
- But it’s not going to happen like that

- Without an active, honest dialogue, without a network of expertise, no-one will make money from nanoparticles
- With a good dialogue and a network the hopes of a mutually successful business are high!
- Maybe AIMCAL can help…