Novel functional additives for advanced coatings and resins

Alan Taylor

Materials Joining and Engineering Technologies

TWI Mission
Who are we?

- A world centre of expertise in Manufacturing, Engineering, Materials and Joining
  - Established in 1946
- Dedicated to supporting the needs of our Industrial Membership
  - Effectively owned by Members and run by representatives from Member Companies
- Non-profit distributing
  - No share holders
  - All income re-invested in the business for benefit of Members

Our Industrial Member Sectors

Construction & Engineering




Aerospace & Automotive

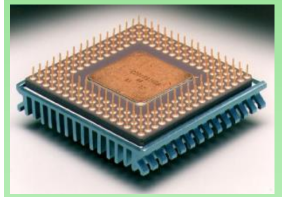
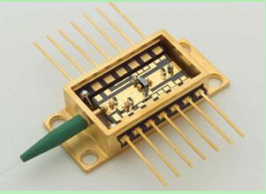



Energy & Environment



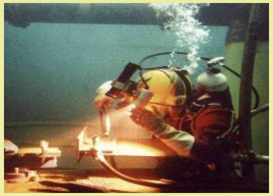

Electronics, Photonics & Medical



Oil, Gas & Chemical



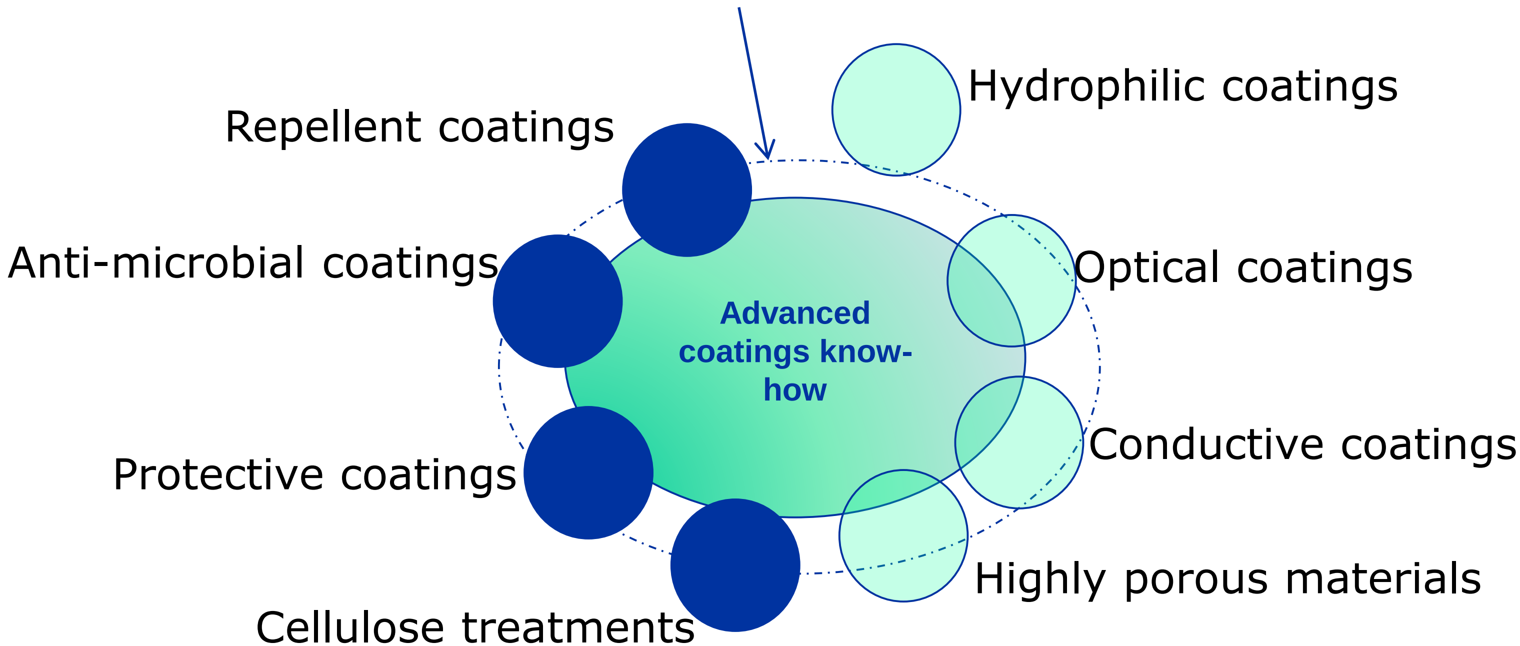



Equipment, Consumables & Materials




Technology overview

Extension of know-how through project work

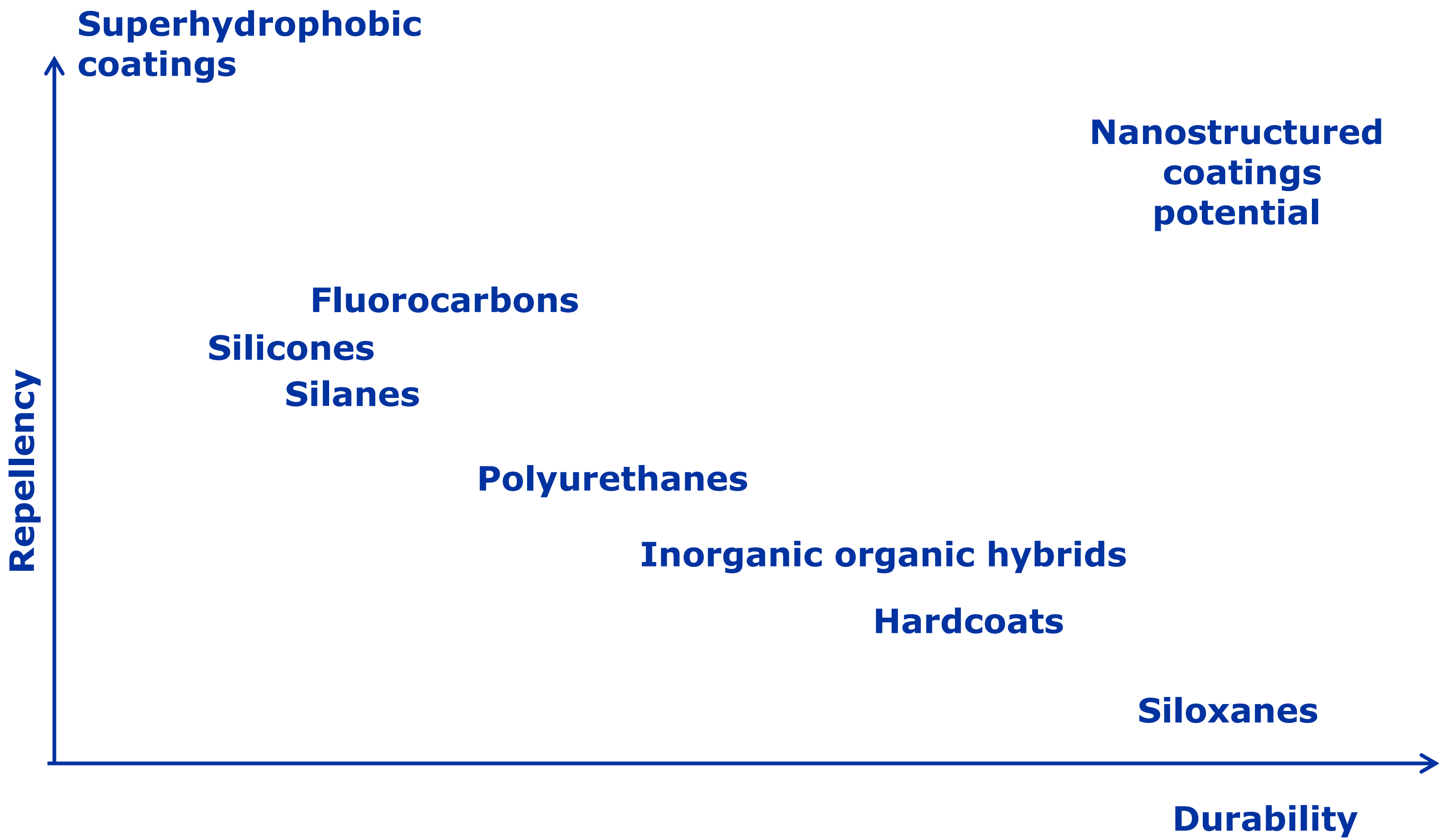


Surface contamination is a significant industrial problem

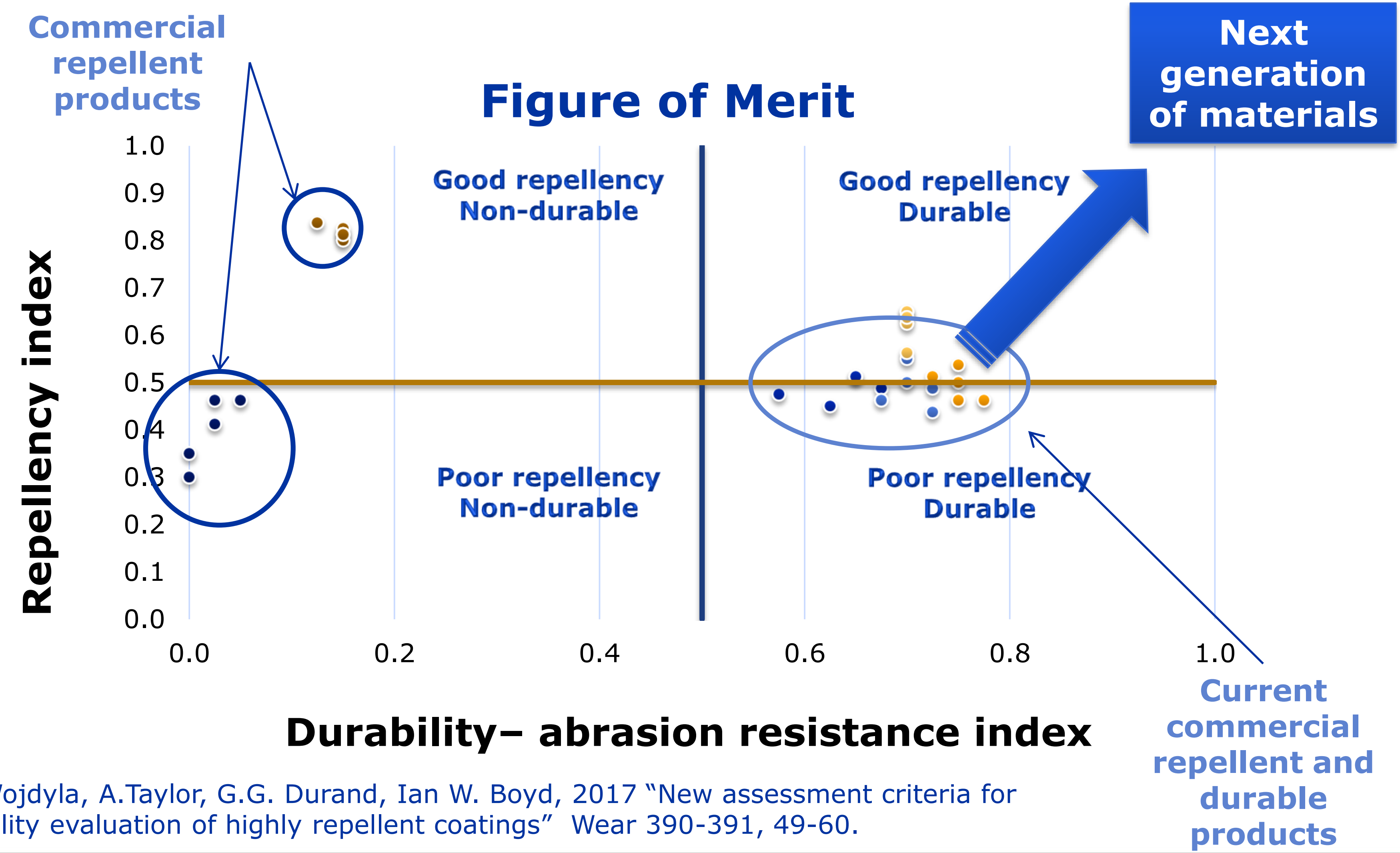
COSTS … MONEY

- **Fouling of surfaces**
  - Increases weight
  - Causes drag
  - Reduces flow
  - Provides sites for corrosion
  - Reduces efficiency
  - Increases emissions
  - Demands cleaning
  - Increases maintenance penalty

Null hypothesis

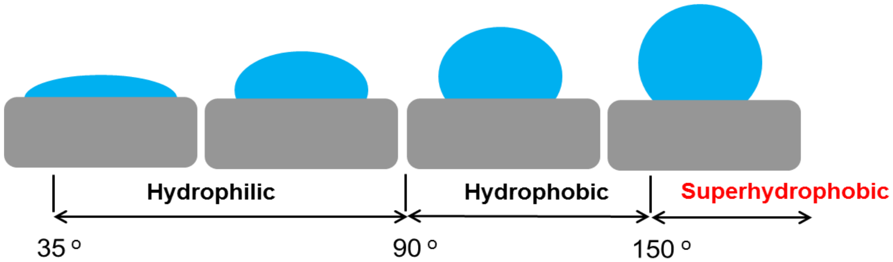


Performance evaluation



A.M. Wojdyla, A.Taylor, G.G. Durand, Ian W. Boyd, 2017 “New assessment criteria for durability evaluation of highly repellent coatings” Wear 390-391, 49-60.

Fundamentals of wetting

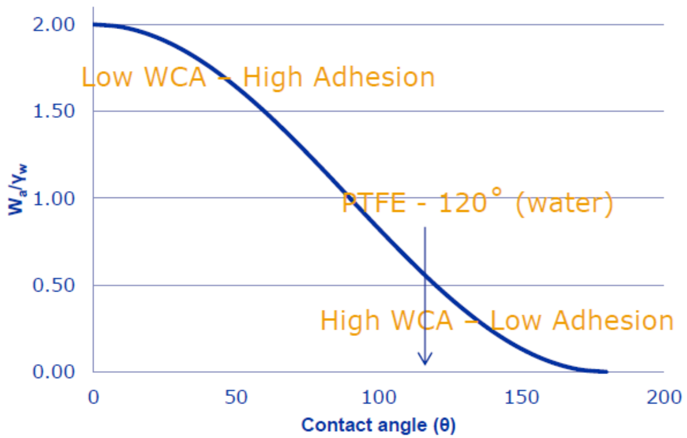


Young Equation

$$\gamma_{sv} = \gamma_{lv} \cdot \cos\theta + \gamma_{sl}$$

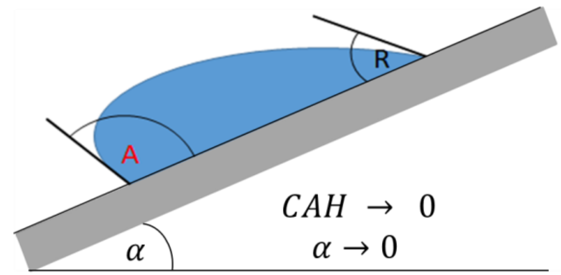
Young-Dupré equation

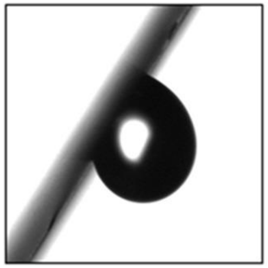
$$W_a \approx \gamma_w (1 + \cos\theta)$$



Makkonen : J Adhesion Sci. Technol. 26 (2012) 413-445

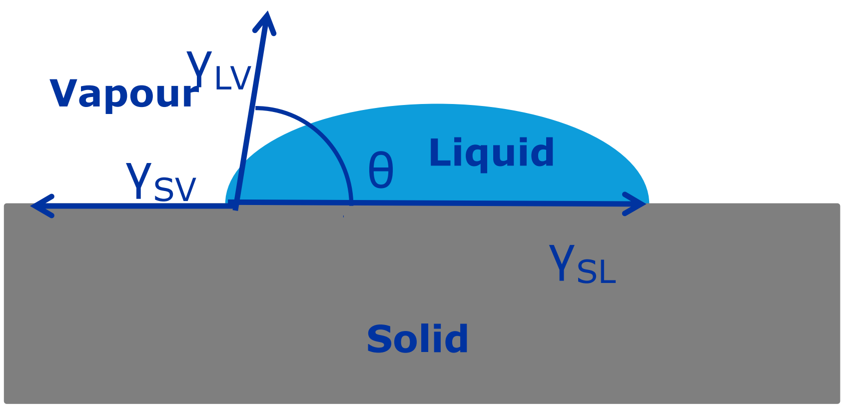
$$CAH = A - R$$





Wenzel equation

$$\cos\theta_{\gamma}^{C} = r \cos\theta\gamma$$



Approaches to create highly repellent coatings

- Structured surfaces
  - Power beam
  - Lithographic
  - Etching
  - Layer by layer deposition
- Additive incorporation
  - CNTs, graphene etc
  - Fumed silica
  - Colloidal silica
  - Functionalised silica
- Sol-gel methods to inorganic-organic hydrids

The need for new additives

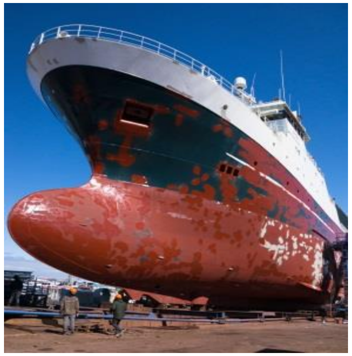
- Management of surface topography
  - Size
  - Shape
  - Degree of aggregation
- Reduction in surface energy
  - Hydrocarbon
  - Fluorocarbon
  - Hydroxyl management
- Enhancement of robustness
  - Cross-linking capability
- Chemical compatibility with film formers

Design strategy

- Performance specification
- Compositional considerations
- Influence of structure and structural hierarchy
- Raw materials selection
- Selection of general synthesis approach
- Fabrication sequence
- Prototype production and evaluation
- Strategy refinement and optimisation
- Scale-up/commercialisation

Core areas for advanced coatings R&D





- **Materials by design**
- **Durable functional coatings and materials**
  - Omni-phobic surfaces
  - Anti-corrosion coatings
  - Anti-microbial
  - Erosion, abrasion & scratch resistant coatings
  - Anti-reflective coatings
- **Recycling**
  - Elemental extraction
  - Polymer purification
- **Nanomaterials**
  - Establishment of design rules
  - Proof-of-principle formulation
  - Synthesis and scale-up
- **Liquid technologies**
  - Solvent replacement
  - Adhesion enhancement
  - Solubility and chemical compatibility



ISOBIO

Development and Demonstration of Highly Insulating, Construction Materials from Bio-derived Aggregates

100% Bio-based materials (UR1)
Green binders
Aggregates (Cavac)

Modified green binder (UR1, CAV)
Green binders with cross linkers
Aggregates and Fibres (Cavac)

Treatment (TWI)
Aggregates and Fibres (Cavac)

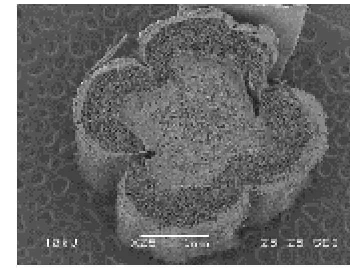
Mineral Foam (UR1)
Thermo® (BCB Binder) or Clay (Claytec)

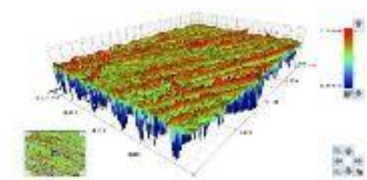
Render and Plaster (UR1, CAV, CLAY and BCB)
Thermo® (BCB Binder) or Clay (Claytec)

Aggregates low density

Aggregates high density

Multilayer insulation panel
- External Layer
- Core
- External Layer





- 4-year project: from February 2015 to February 2019
- 6.3 M€ European grant (№ 636835)
- 12 partners from 6 EU countries
- http://isobioproject.com

WELDAPRIME

Self-repairable Zinc-free Weldable Anti-corrosion Primer for Steel Protection

Rust develops on steel during transportation, handling and storage.
→ Material waste and higher costs

Development of an anti-corrosion weldable, zinc free primer that lasts at least 1 year and that does not need grinding before welding or blast-cleaning before finishing.

Coating development aspects:

- Synthesis
- Formulation
- Deposition and curing
- Testing
- Demonstration

Application of sol-gel derived materials to address:

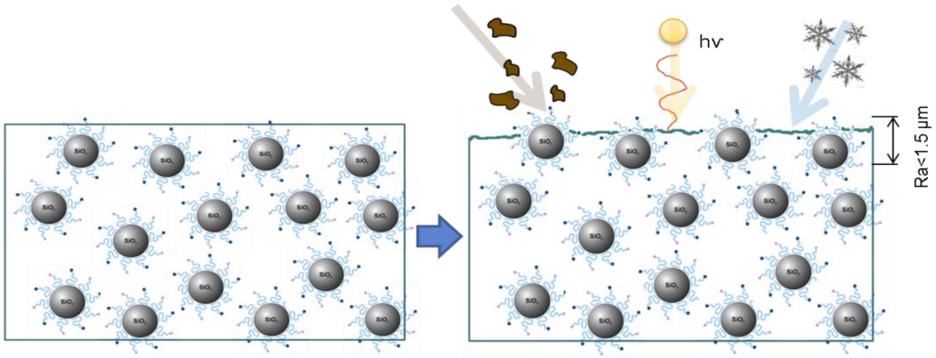
- Corrosion performance
- Weld-through characteristics
- Compatibility with the final top-coat (applied to the welded structure)
- Low VOC and Zinc-free

EIROS

Ice and Erosion resistant Composite structures

Development of a high performance composite material by incorporating innovative additives into the composite bulk matrix for operation in extreme environments

- ✓ Increased erosion resistance
- ✓ Anti-icing characteristics
- ✓ Self-healing properties



Improved impact resistance of resin and particle distribution

Functional groups at surface give erosion/ice resistant surface

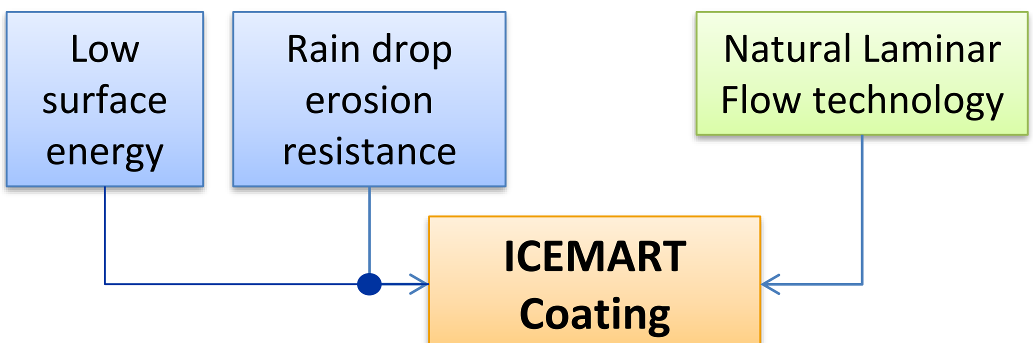
ICEMART

Durable ice-repellent laminar flow coatings for the aerospace sector

The ICEMART project will develop an ice-repellent coating to prevent or minimise ice formation and adhesion without the need of active ice-management systems

Wide impacts:

- ✓ Advances in flight safety
- ✓ Reduction of de-icing power needs/weight (↑ efficiency, ↓ CO_2 emissions)
- ✓ Reduce drag (↑ fuel efficiency)
- ✓ De-icing on-ground costs and environmental impact ↓ (de-icing liquids)



SolarSharc™

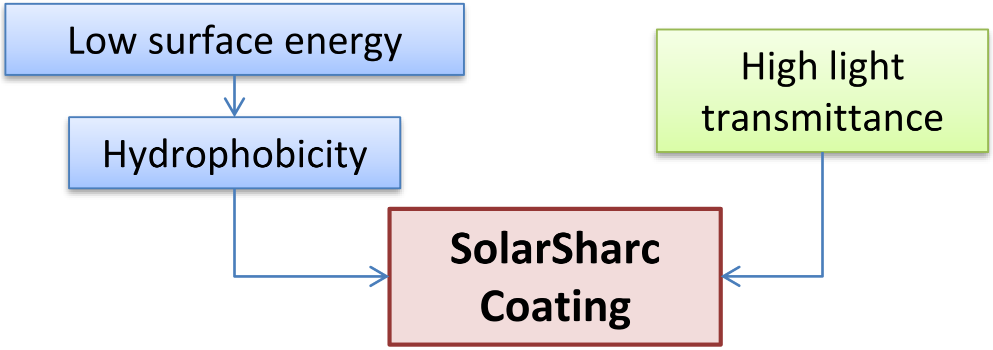
Improved Energy Efficiency of Solar PV Systems via Low Surface Energy Coatings

Accumulation of dust/soiling can cause reductions in peak power of ~15% in many locations, and as high as **50%** in some dusty areas.

Source: PolyWater® corporation

The SolarSharc solution: A novel durable highly repellent coating based on advanced, low energy material that can provide a permanent solution to PV systems

- ✓ Reduces the power losses due to the build-up of contamination on the solar modules
- ✓ Reduces maintenance costs by reducing the need for regular cleaning.



Materials & additives design

Our Aim: Using **State of the Art Technology** and **TWI Know How** to modify your current product or process to improve performance.

- Additives Design
- Solvent Design

Molecular Design

Incorporation Process optimisation

- Resin incorporation
- Process optimisation
- Material stability

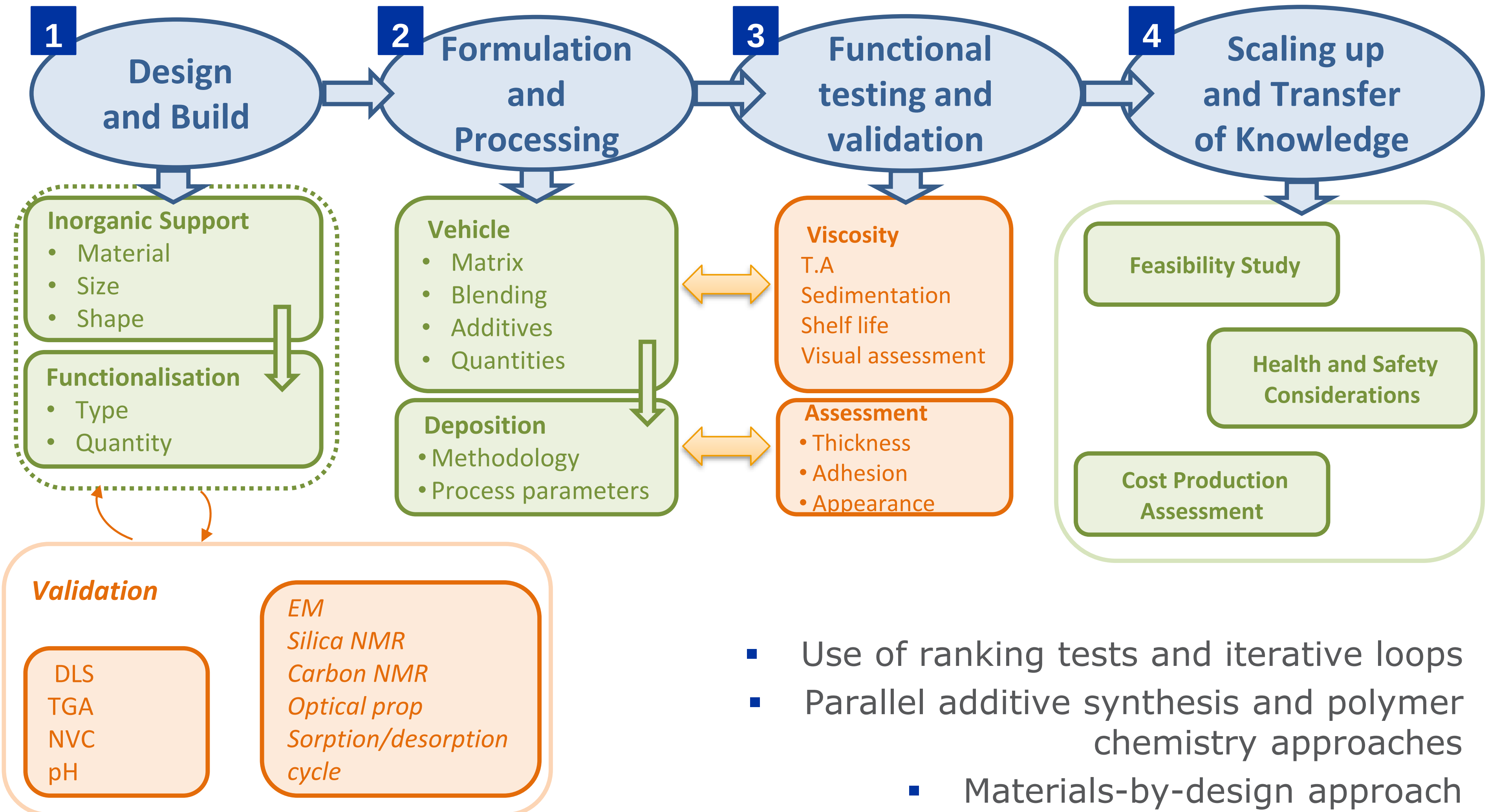
Solvent End of Life Recycle

- Polymer dissolution and Recycling
- Ionic liquids
- LCA

Performance Evaluation

- Characterisation
- Comparison to SoA
- Fit for purpose

General approach

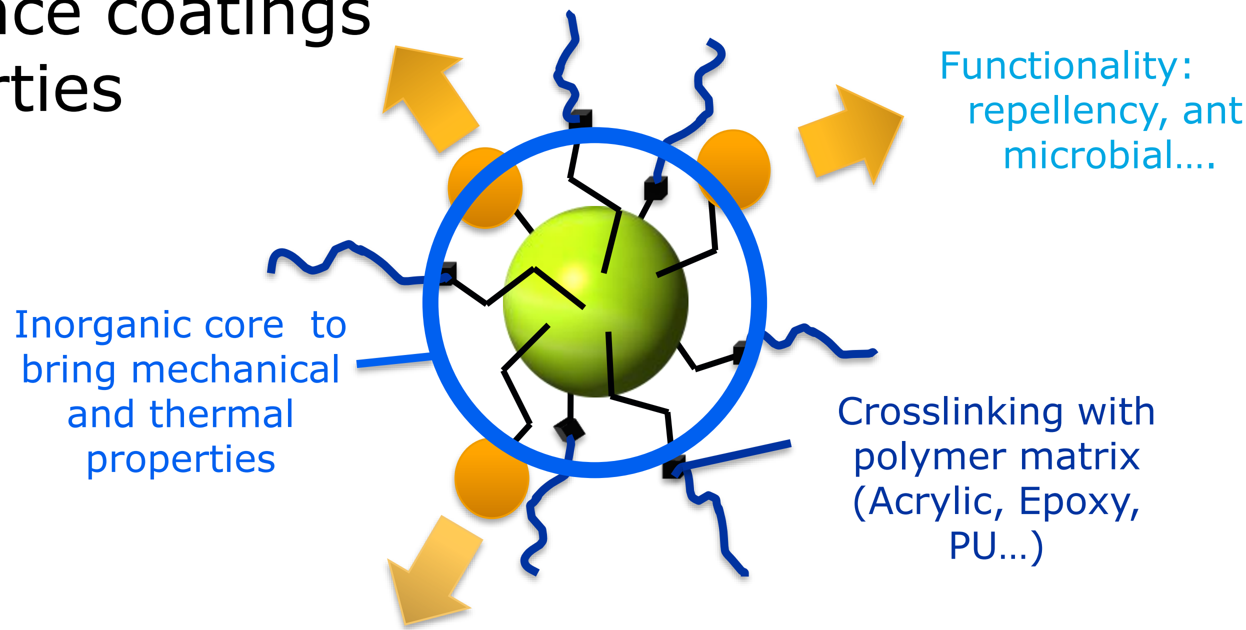


- Use of ranking tests and iterative loops
- Parallel additive synthesis and polymer chemistry approaches
- Materials-by-design approach

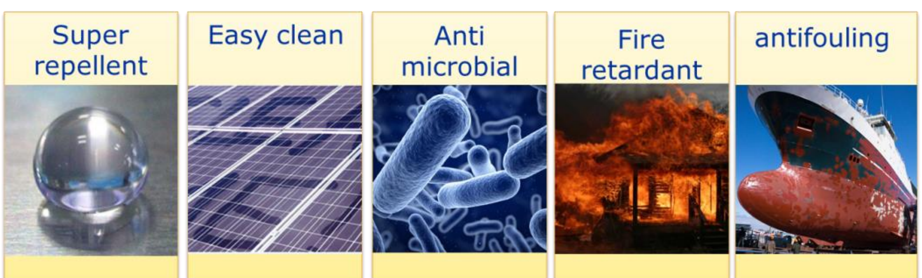
Materials-by-design

Additive to enhance coatings and resins properties

Unique methodology which allow dual functionalisation of nanoparticles

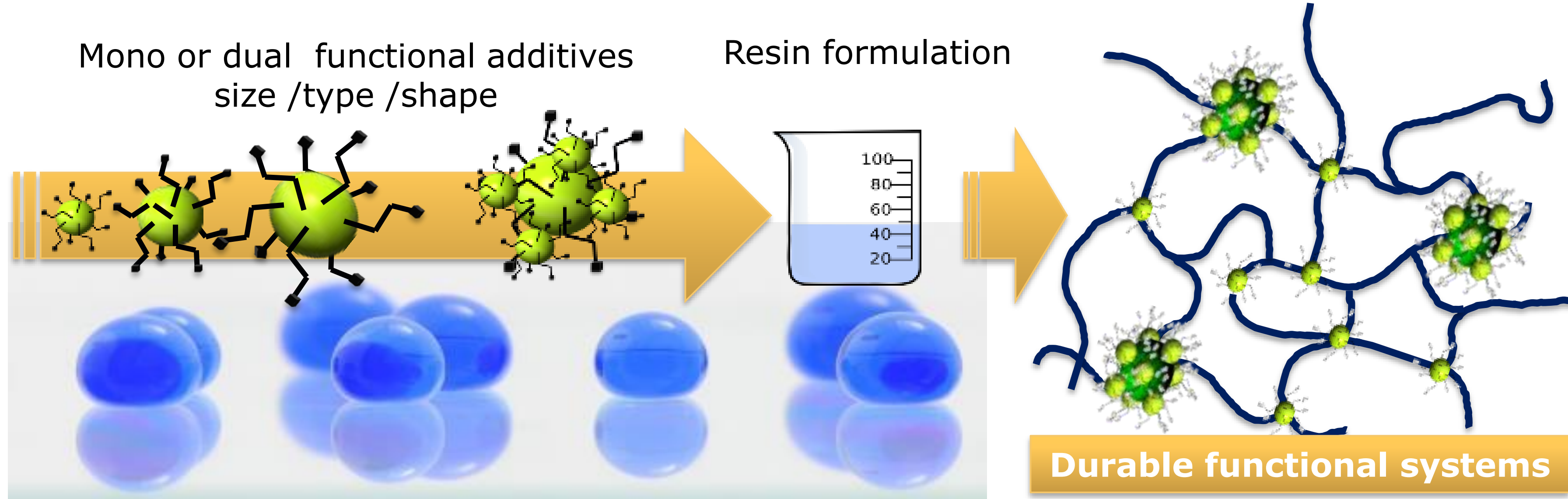


Various functionalities

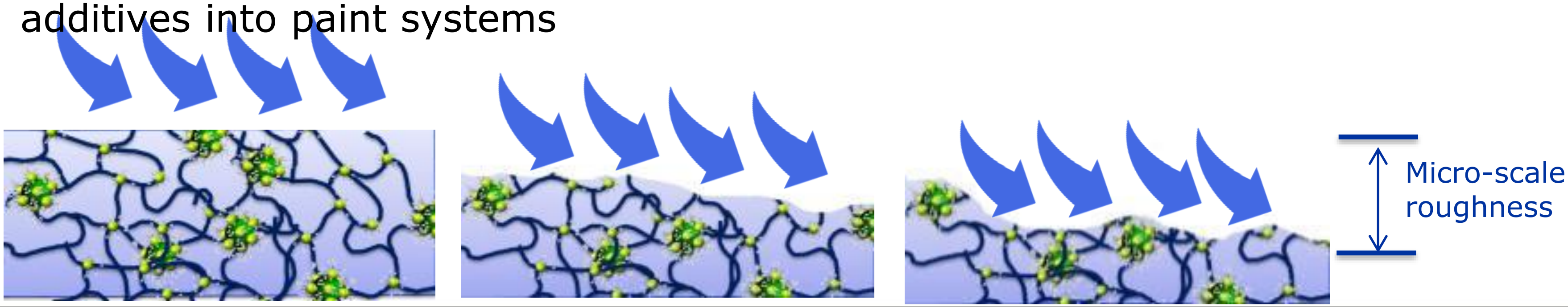


Various substrates

Materials-by-design approach
Functional coating design



Development of high performance hybrid materials by incorporating novel additives into paint systems



Stöber synthesis of silica particles

Part A

Alcohol + TEOS

Part B

Alcohol + water + ammonia

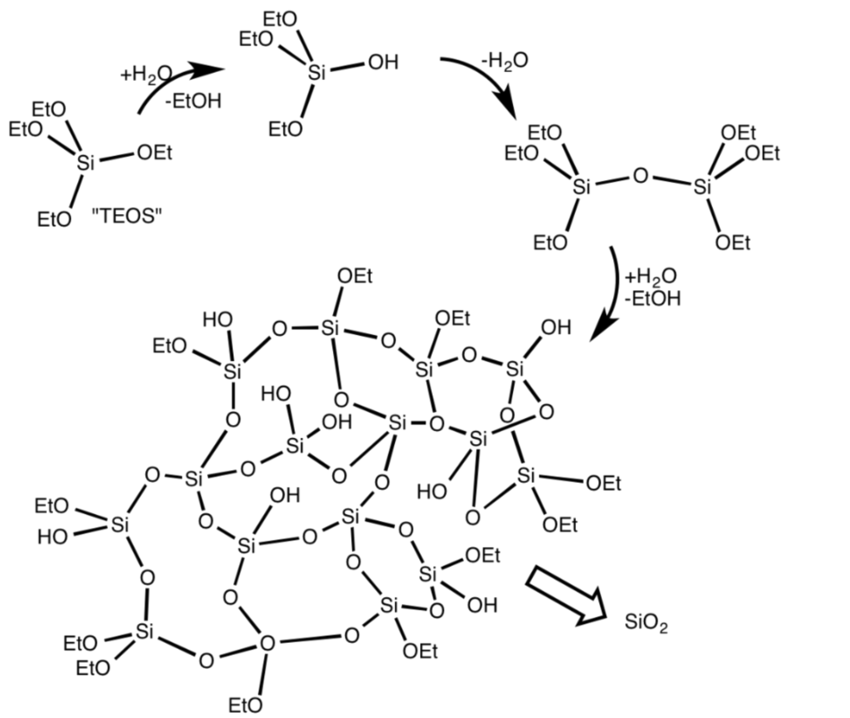
Mix for 1-2 minutes

Combine

Age

Cleaning

TSSx

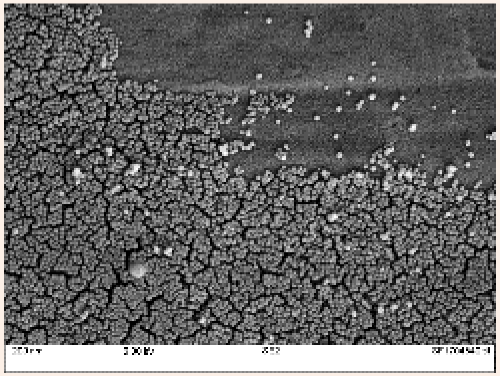


Characterisation of Stöber silica

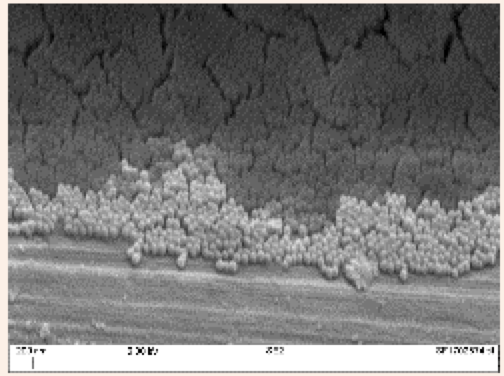
Methodology	Output	TSS4	TSS11	TSS12	TSS21	TSS22	TSP22
DLS/SEM	Z-average (d.nm)	20-35	115-125	160	110-115	155-170	250-300
	PdI	0.2	0.1	0.1	0.08	0.05	0.06
NVC (%)	Solid content (%)	4.3	4.2	4.2	4.2	4.1	4.2
BET Surface Area	Surface Area (m^2/g)	340	210	220	80	50	20
	Micro-/ meso-porosity (nm)	1.1-8.7	1.5-40	0.8-25	2.4-43	2.8-65	2.9
	Total Pore Volume (cm^3/g)	0.38	0.35	0.38	0.27	0.26	0.23

Stöber silica particles

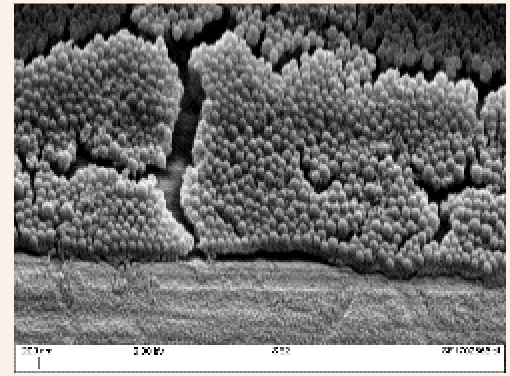
TSS4



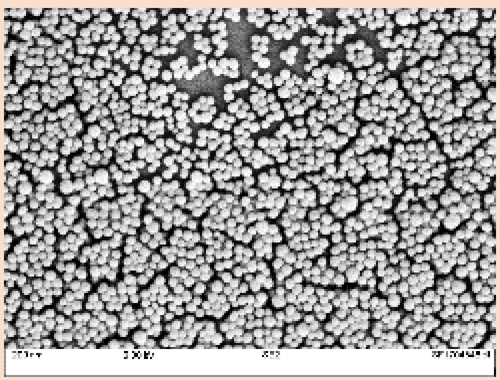
TSS11



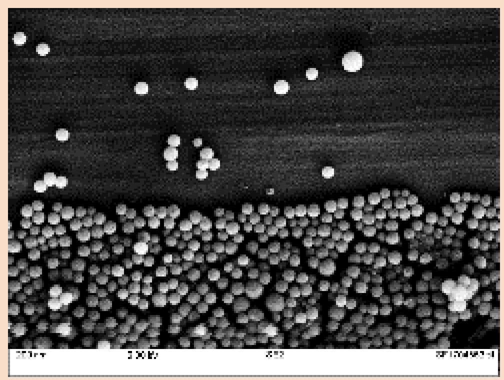
TSS12



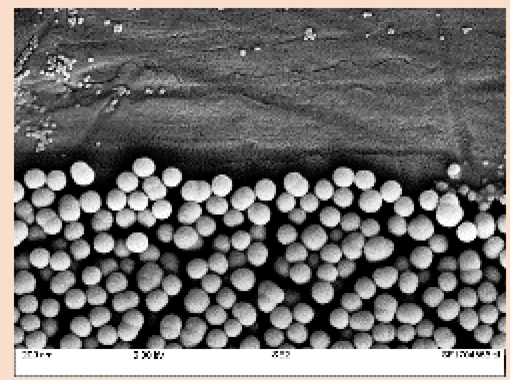
TSS21



TSS22



TSP22

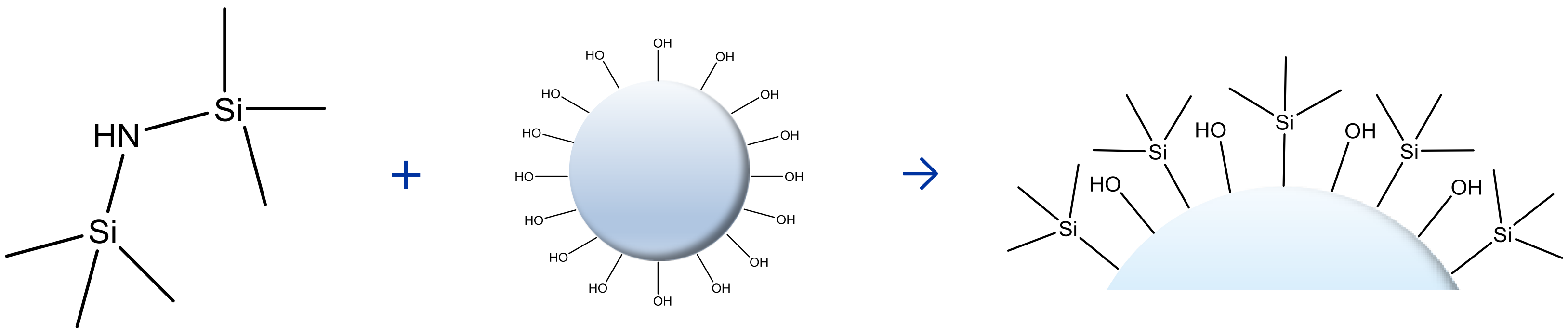


SEM image of TSxx dip-coated on an aluminium slide (scale 200nm).

Silica particle fabrication

- Simple mixing process
- Particle size controlled by initial solution chemistry
- Retention of primary particles (no aggregation)
- Solvent based mixture
- Scale-up possible
- Tolerant to hydrolytically sensitive functionalisation agents

Silica functionalisation

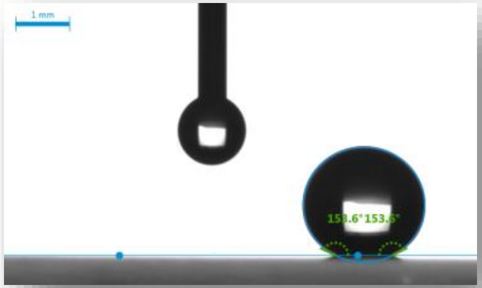


- Functionalisation agent
- Relative quantities - silica/agent
- Reaction conditions
- Use of catalyst
- Validation/verification
- Functional efficacy

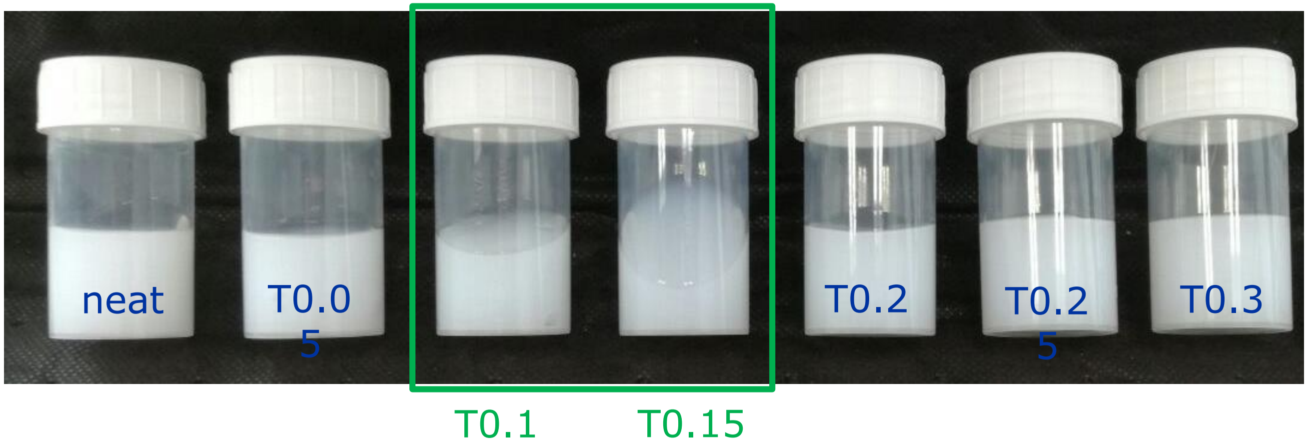
Nanoparticle functionalisation: Developing repellency

		TSS4	F333	NPTMS	HMDS	NFHTMS	NFHDMMS
Contact Angle	WCA [°]	34.4	131.7	119.8	150.2	139.2	118.3
	DCA [°]	30.1	114.3	60.9	99.9	130.7	71.9
DLS	Particle size (nm)	30.9	43.8	43.38	49.74	44.16	43.68
	PdI	0.171	0.236	0.14	0.05	0.13	0.082
NVC [%]		4.3	6.61	6.7	4.45	6.09	6.35

HMDS: hexamethyldisilazane
N-propyl: n-propyl trimethoxy silane
F333: 3,3,3 trifluoropropyl silane
NFHTMS: (3,3,4,4,5,5,6,6,6 nonafluorohexyl)trimethoxysilane
NFHDMMS: (3,3,4,4,5,5,6,6,6 nonafluorohexyl)dimethylmethoxysilane



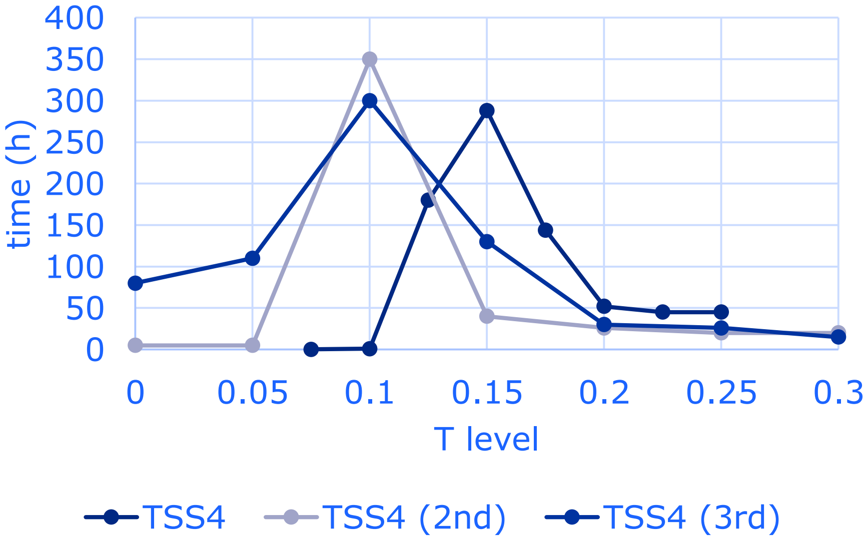
Monolayer study - Gelling time



$$T_{level} = \frac{m_{silane}}{m_{TSS4}}$$

Protocol used: TSS4@NPTMS + NH_4OH (ratio 4:1)

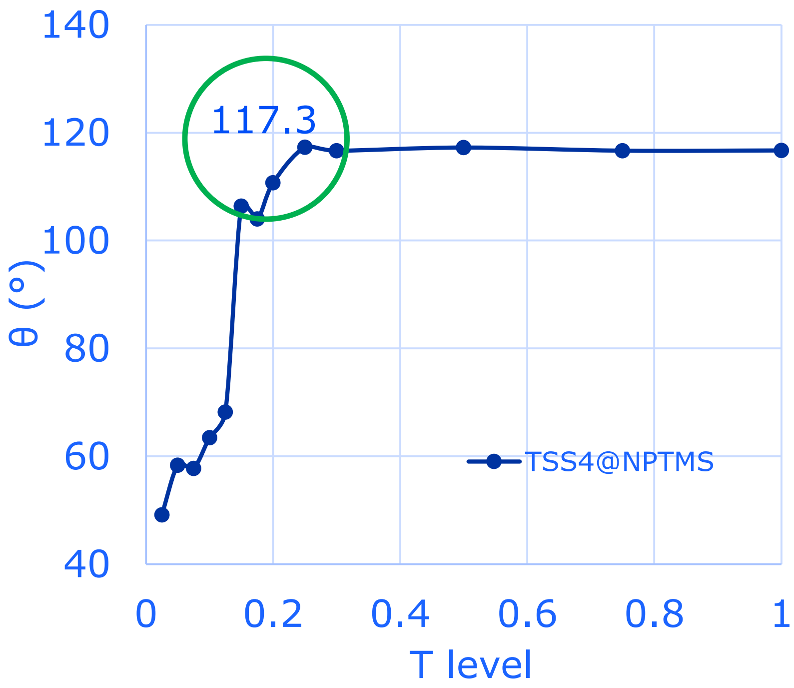
Visual observation of gelling phenomena (above) and graph of gelling time (right) of TSS4@NPTMS samples at T level between 0 and 0.3 (above)



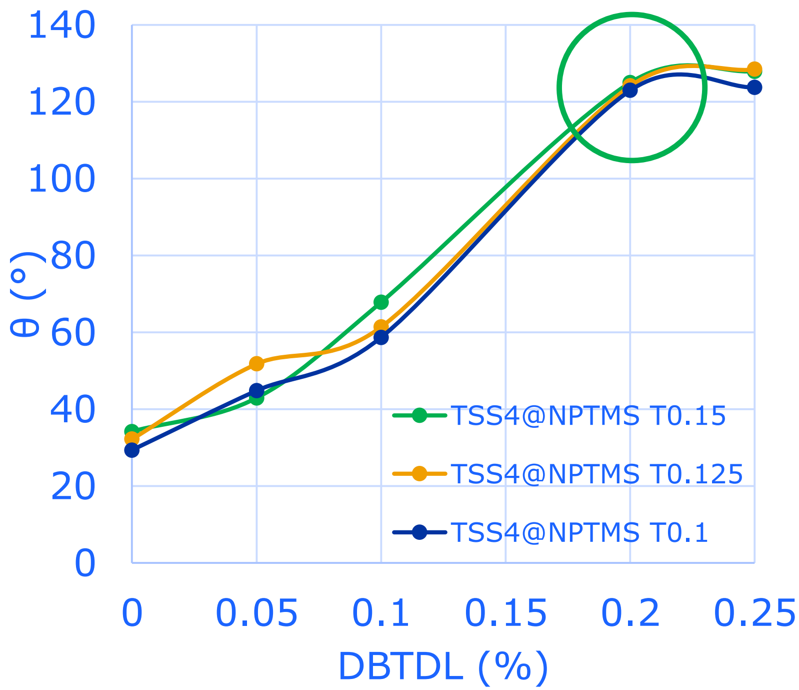
Monolayer study – DSA analysis

Optimisation of silane level and catalyst

Influence of coverage



Influence of catalyst



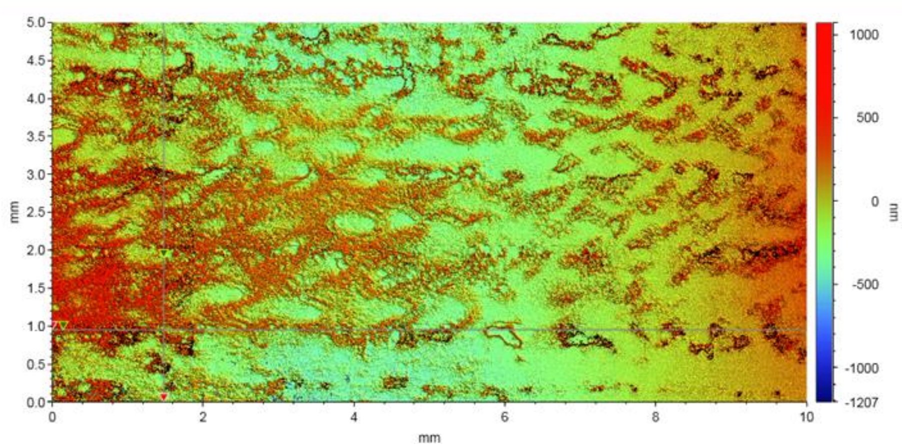
Topographic considerations

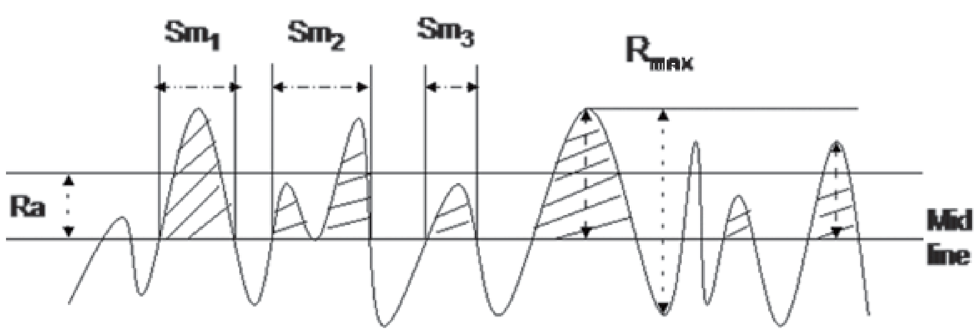
There are more than 40 roughness parameters

$$R_a = \frac{1}{L}\int_0^L |Z(x)|\,dx$$

$$R_q = \sqrt{\frac{1}{L}\int_0^L |Z^2(x)|\,dx}$$

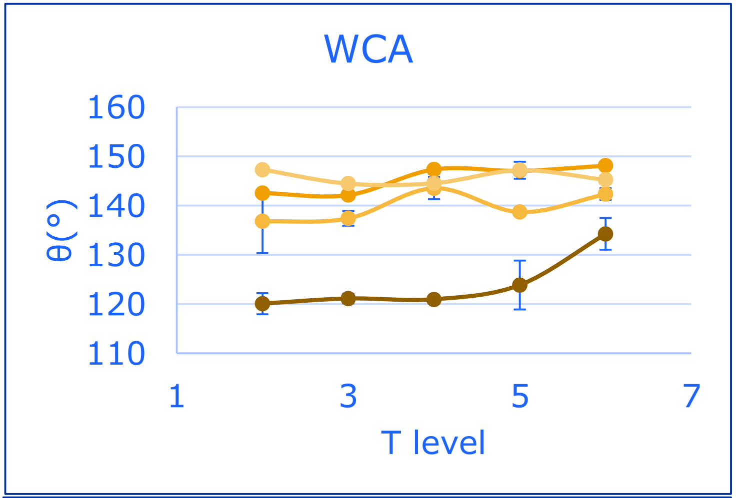
$$F = 2\pi\omega R\left[\frac{R_q}{R+R_q} + \left(\frac{h_c}{h_c+R_q}\right)^2\right]$$

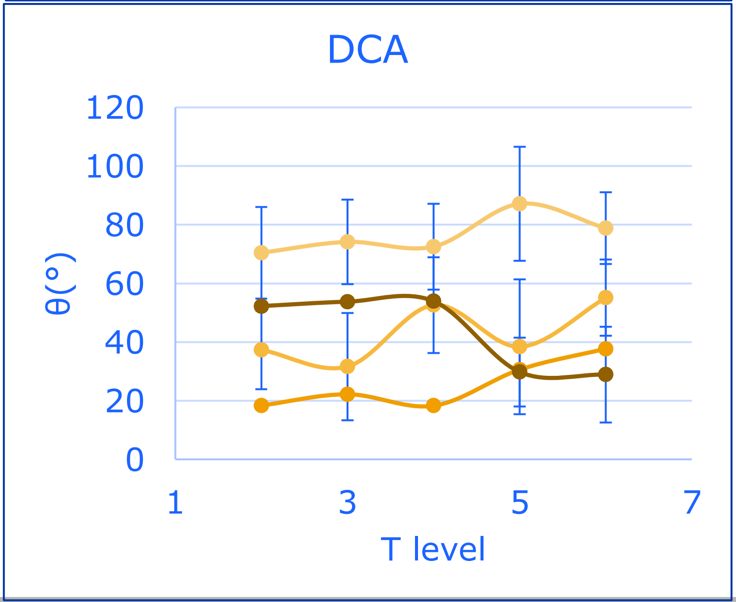


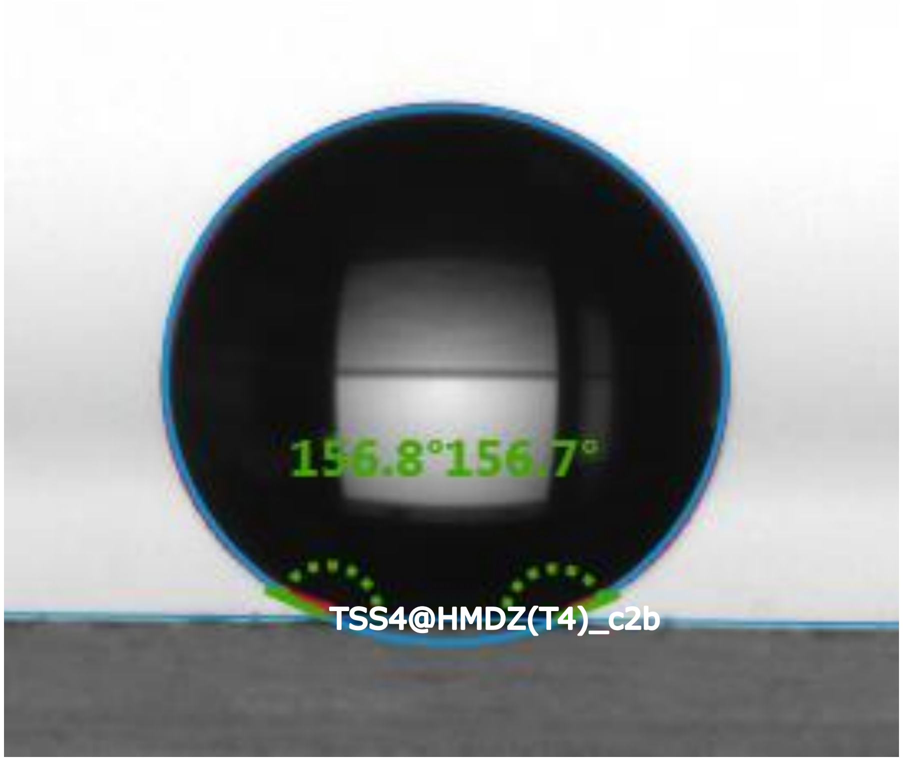


Which parameters drive Behaviour?

Approach to omniphobic materials







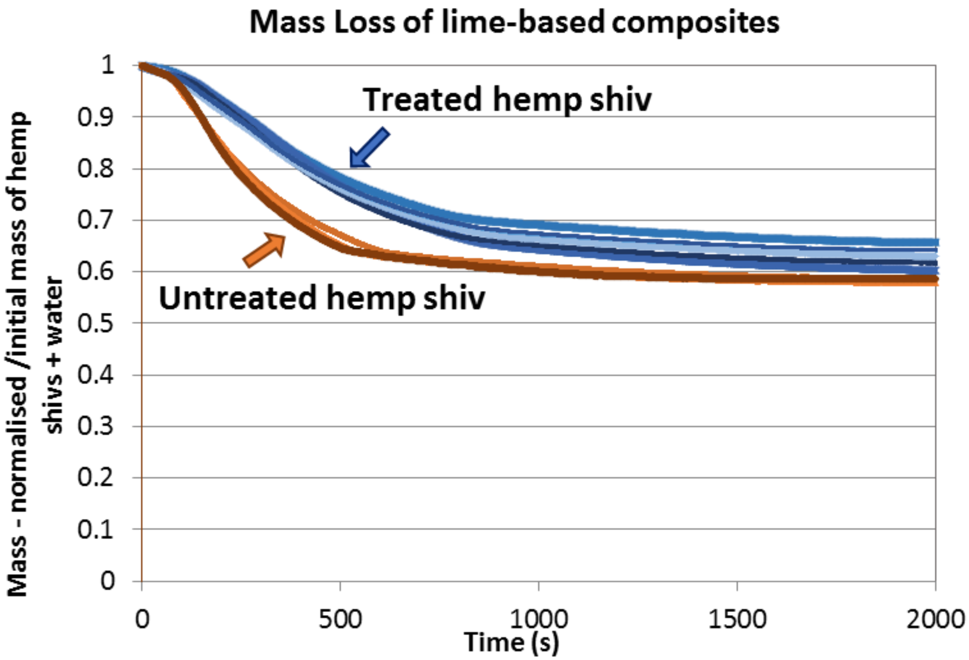
Functionalised silica particles

Bourebrab, M.A.; Durand, G.G.; Taylor, A. Development of Highly Repellent Silica Particles for Protection of Hemp Shiv Used as Insulation Materials. *Materials* **2018**, *11*, 4.

Improved performance …

Water repellence

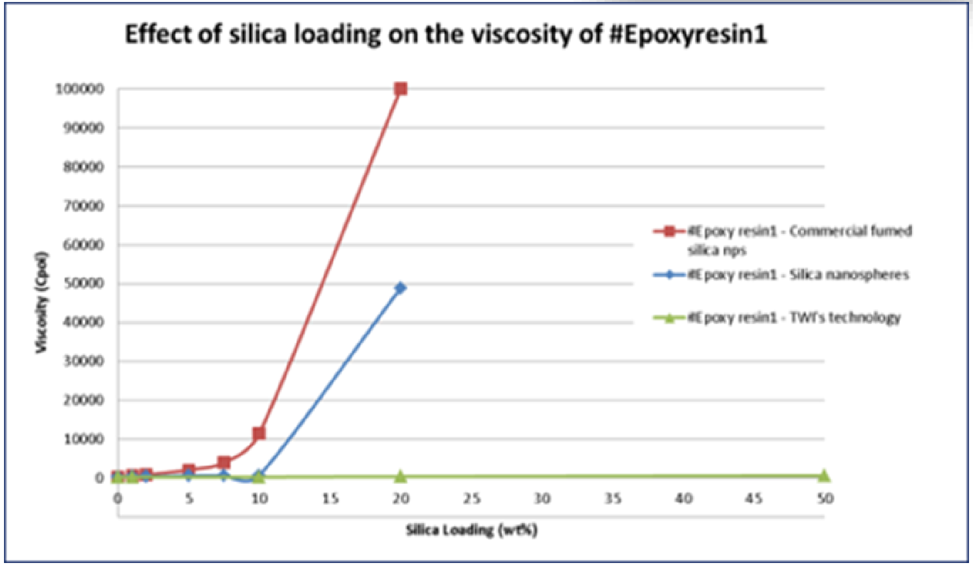
Fire retardance



Formulation into resins

- Surface functionalisation of the particle prevents agglomeration and minimises viscosity increase

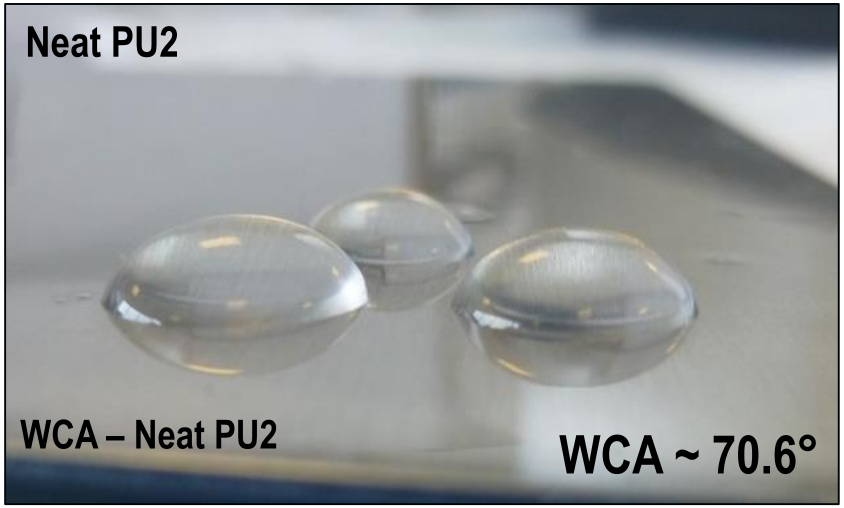
- Incorporation of inorganic core additives into liquid resin system at high loading levels without significant change in viscosity is possible

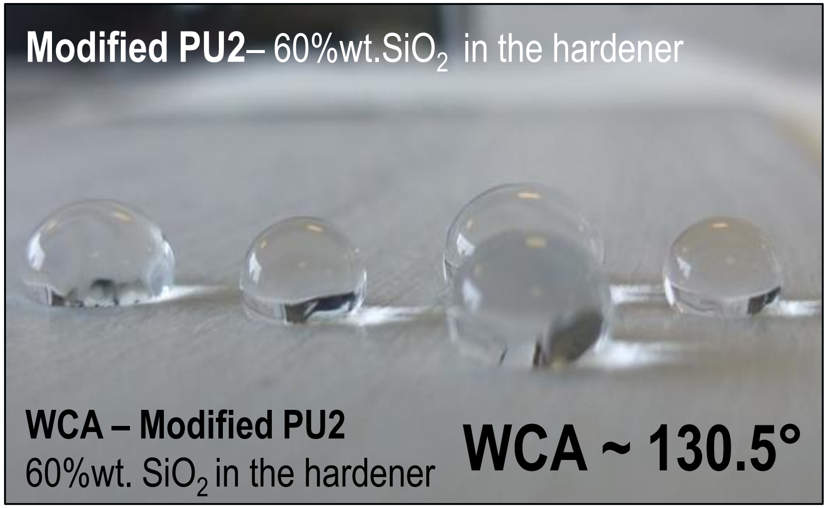


Polyurethane matrix coatings

P O L Y U R E T H A N E

Low energy PU coating with abrasion resistant properties using PU from QPL lists



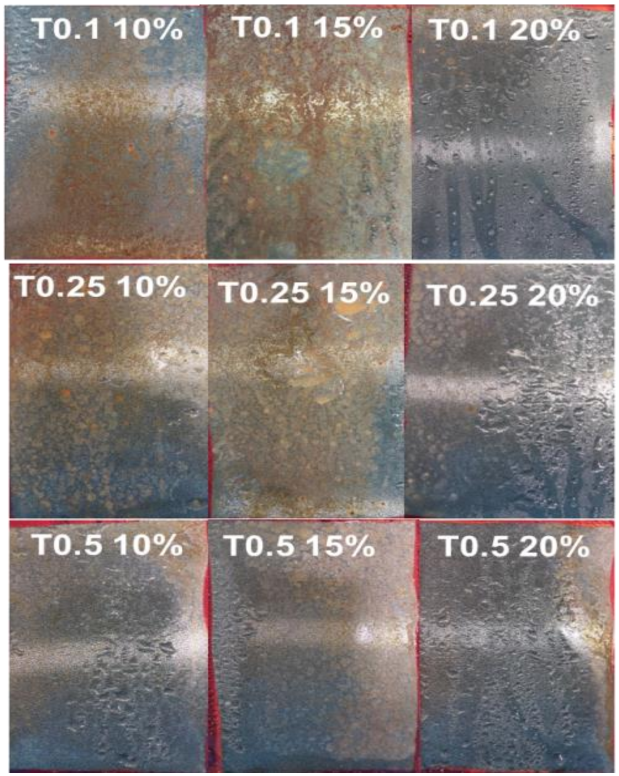


Polysiloxane(I) matrix coatings

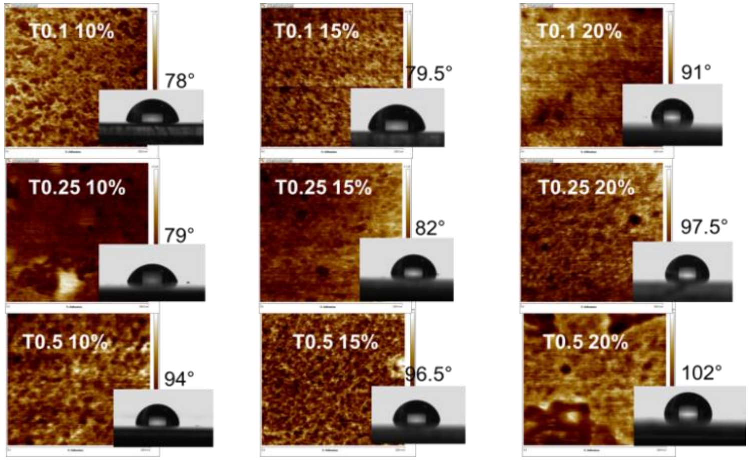
Three functionalisation levels (T0.1, T0.25, T0.5), with nanoparticles incorporated at different loading levels (10%, 15% and 20% wt).

Loading level →

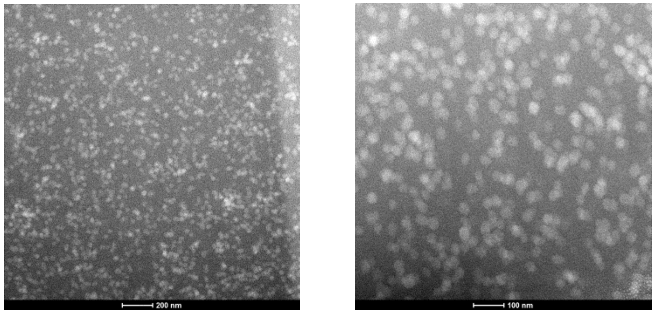
Functionalisation level ↓



Salt spray testing up to 96h

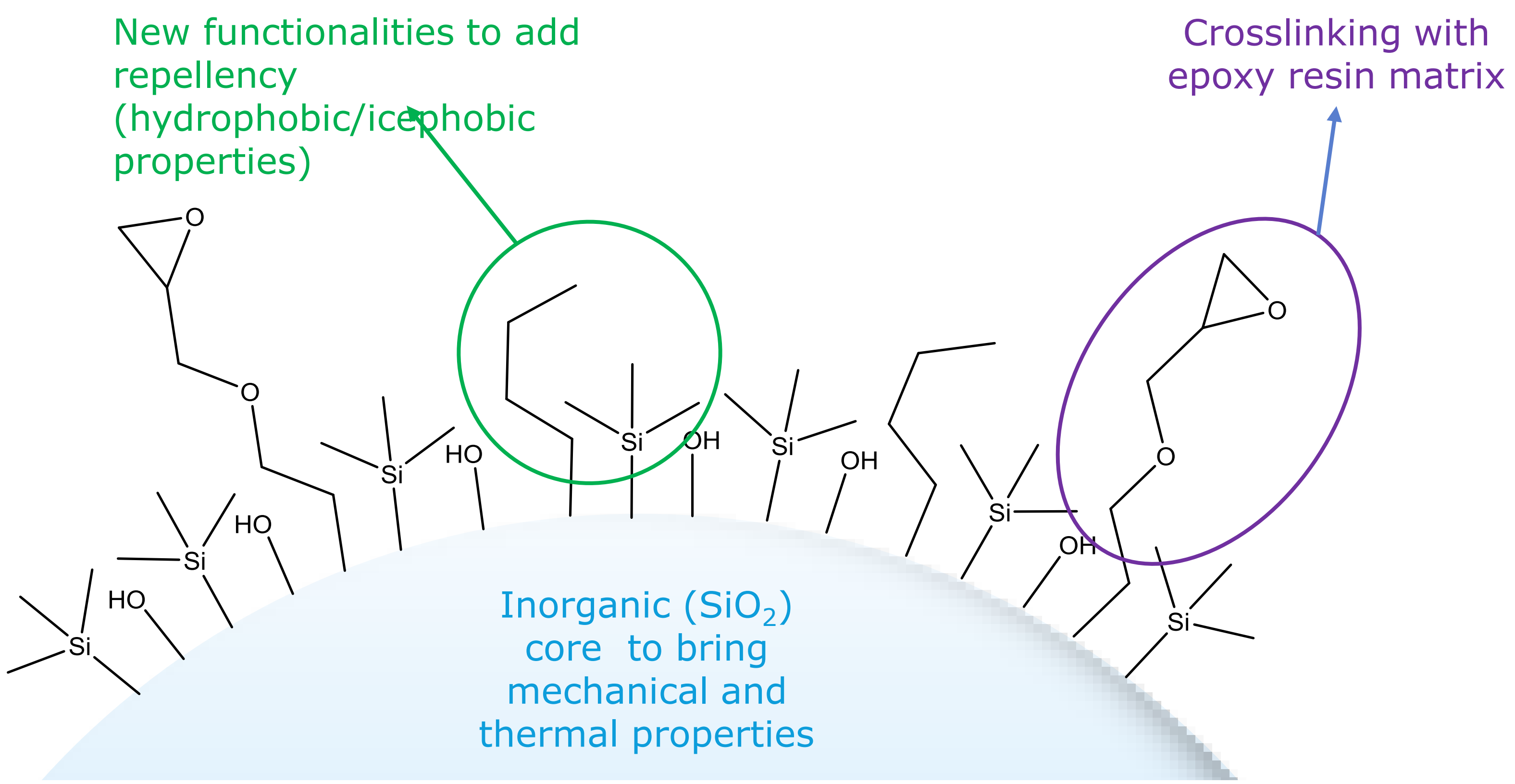


TEM images



Vivar Mora L, Taylor A, Paul S, Dawson R, Wang C, Taleb W, Owen J, Neville A, Barker R, 2018. Surface and Coatings Technology, 342, 48-56

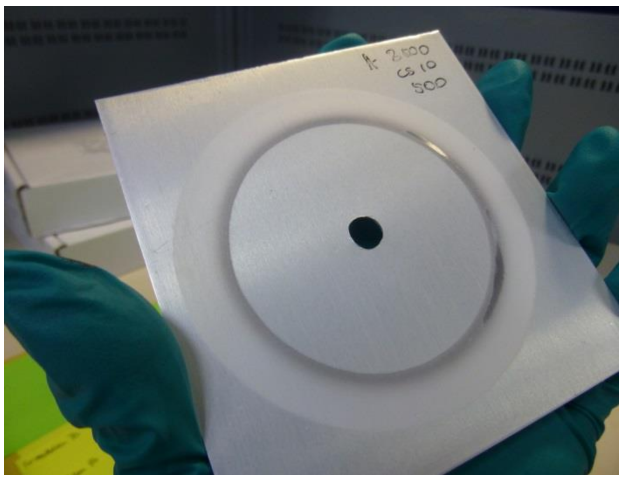
Multi-functionalised particles



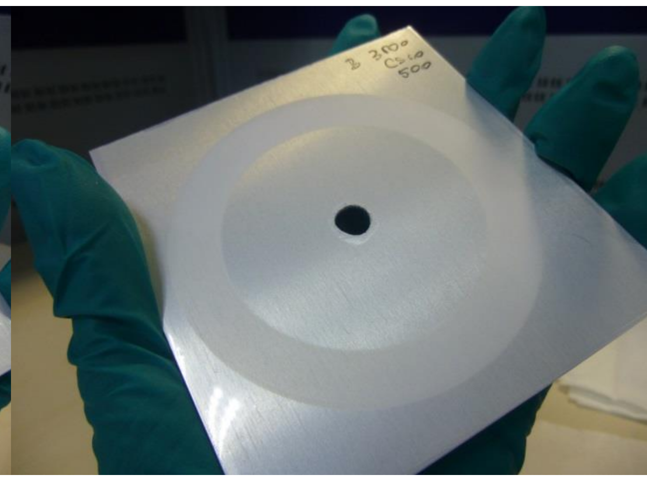
Acrylate matrix coatings

Taber rotary abrasion test

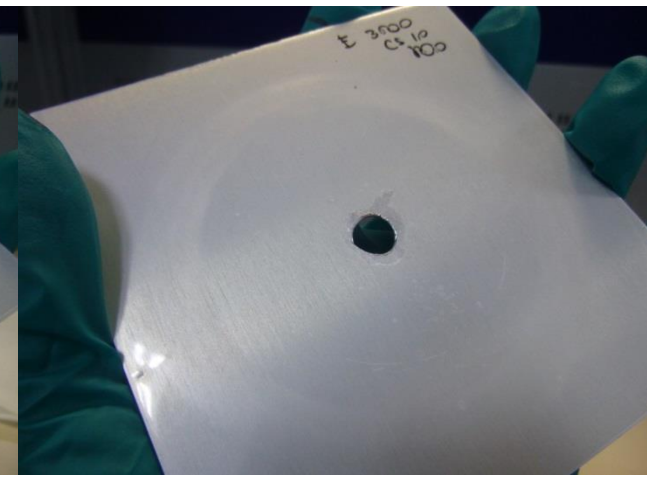
- 3500 cycles (almost 1h of abrasion)
- CS10 wheels
- 500g load on each wheel



Bare Acrylate



Acrylate
+ VitoSil®



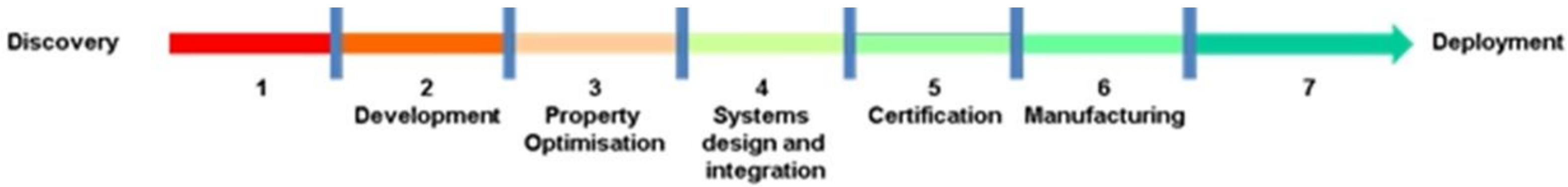
Acrylate
+ VitoSil®
+ VitoNano®

Polysiloxane matrix (II): SolarSharc™

	Glass	SOL+ coated glass
DOI	96.5	97.2
Transmittance (%T)	91-92%	92-93%
Reflectance (%R)	8-9%	5-6%
Water Contact Angle (WCA)	20º	128.8º
Diiodo Contact Angle (DCA)	50º	104.9 º
Thickness	N/A	1-2µm
Abrasion resistance (100 cycles, CS8 wheel, 500*2 loading)		
− WCA after abrasion	N/A	105.79 º (16%) Partial degradation
− Transmittance after abrasion	N/A	91-92% (slight degradation)
Sand impact Test (SIT) (The sample holder 45º, 500 gr of sand in 80 to 100 seconds.)		
− WCA after sand impact test	N/A	112.39 (10.9%) Partial degradation
− Transmittance sand impact test	N/A	90-91% (slight degradation)
UV exposure resistance (500 hours)		
− WCA after UV exposure	N/A	98.7º (-7%) Low degradation
− Transmittance after UV exposure	N/A	92-93% (no impact)
High temperature (85ºC) and High Humidity (85%) exposure resistance (1000 hours):		
− WCA after HT and HH exposure	N/A	84º (-21%) Partial degradation
− Transmittance after HT and HH exposure	N/A	92-93% (slight improvement)
Thermal cycling resistance (-40ºC to 85ºC, 200cycles)		
− WCA after thermal cycling	N/A	102 º (-4%) Low degradation
− Transmittance after thermal cycling	N/A	92-93% (no impact)

New materials: Drivers and challenges

- REACH
- Environmental legislation
- Energy costs
- Security of supply



Materials development continuum (NSTC (2011))

- Industrial adoption
- Customer education
- Market acceptance
- Competitive supply

Conclusions

- Durable, highly repellent surfaces are a key unmet need
- A novel, disruptive approach to materials development is required to address this need
- A new approach to functionalised silica based additives has been adopted
- Integration of functionalised silica into a range of film forming matrices has been carried out
- The design rules for the additives and for coatings containing these additives are being established

Conclusions

- Vertically integrated supply chains within public funded projects have been established
- Scale-up to multi-kilogram levels has been undertaken by multiple partners
- Product development of the additives, coatings and nano-enabled composite materials continues
- S,H & E considerations are being actively investigated
- Commercialisation of the additives is now underway (www.sharcmatter.com)

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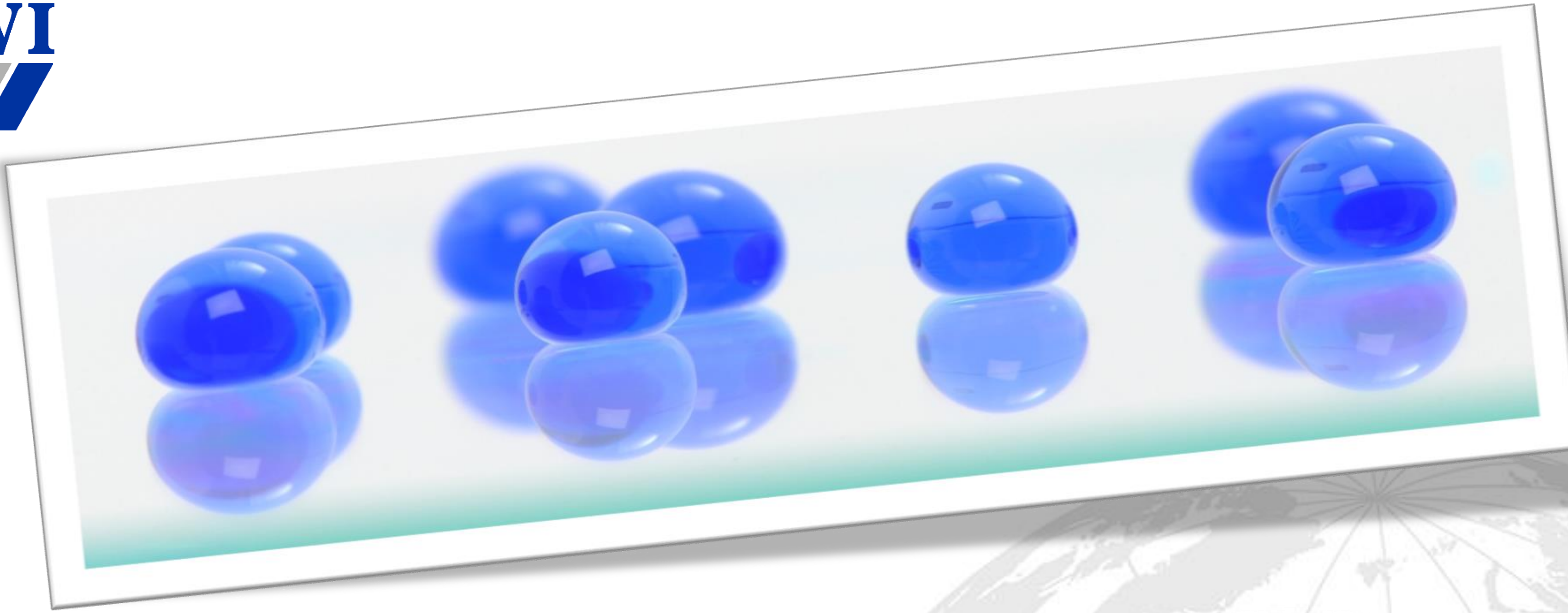

Thank you!

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