Particle Adhesion/Cohesion – A Surface Energy and Wettability Perspective

iGC-SEA

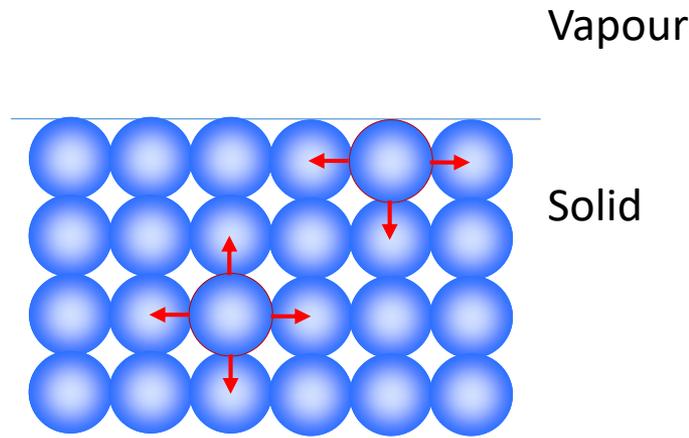Surface Measurement Systems, Ltd.

Dburnett@surfacemeasurementsystems.com

- **Analogous to surface tension of liquids**

- **To quantify the ability of the surface to react** compared to the bulk

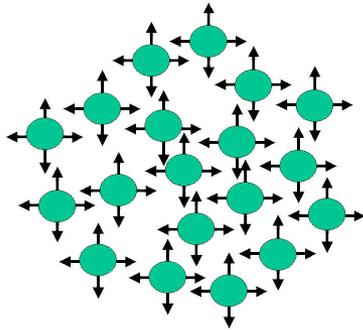- Directly related to the thermodynamic work of adhesion

Vapour

- Surface e   nes:

    - Intermolecu   Solid   common interface

    - Total surface   partially
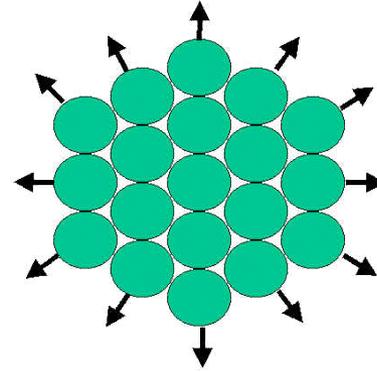   independent   istinctly different
      type of inter

Atoms in the centre of a material are surrounded by other atoms

some of the surface electrons could interact with atoms surrounding the material.

To quantify the ability of the surface to react.

Thermodynamic law: "all systems try to reach their lowest energy levels."
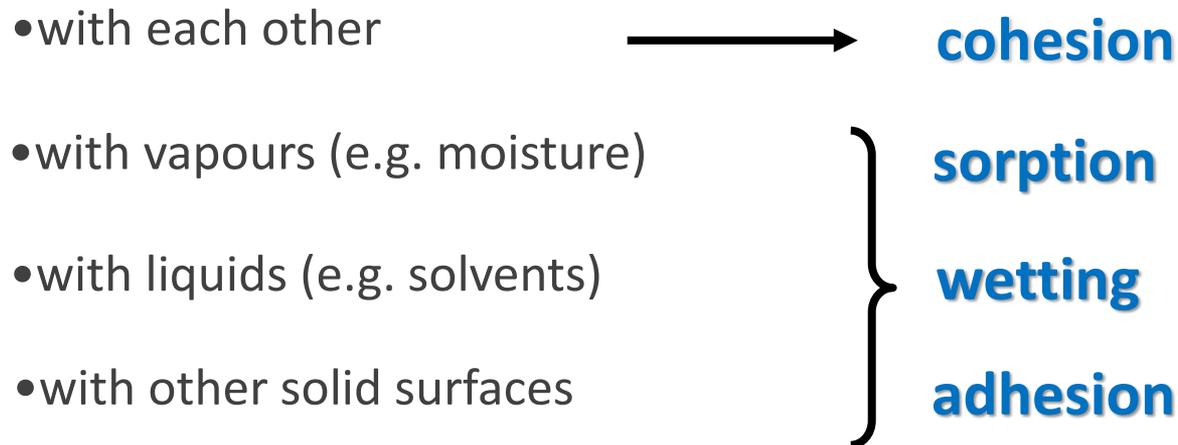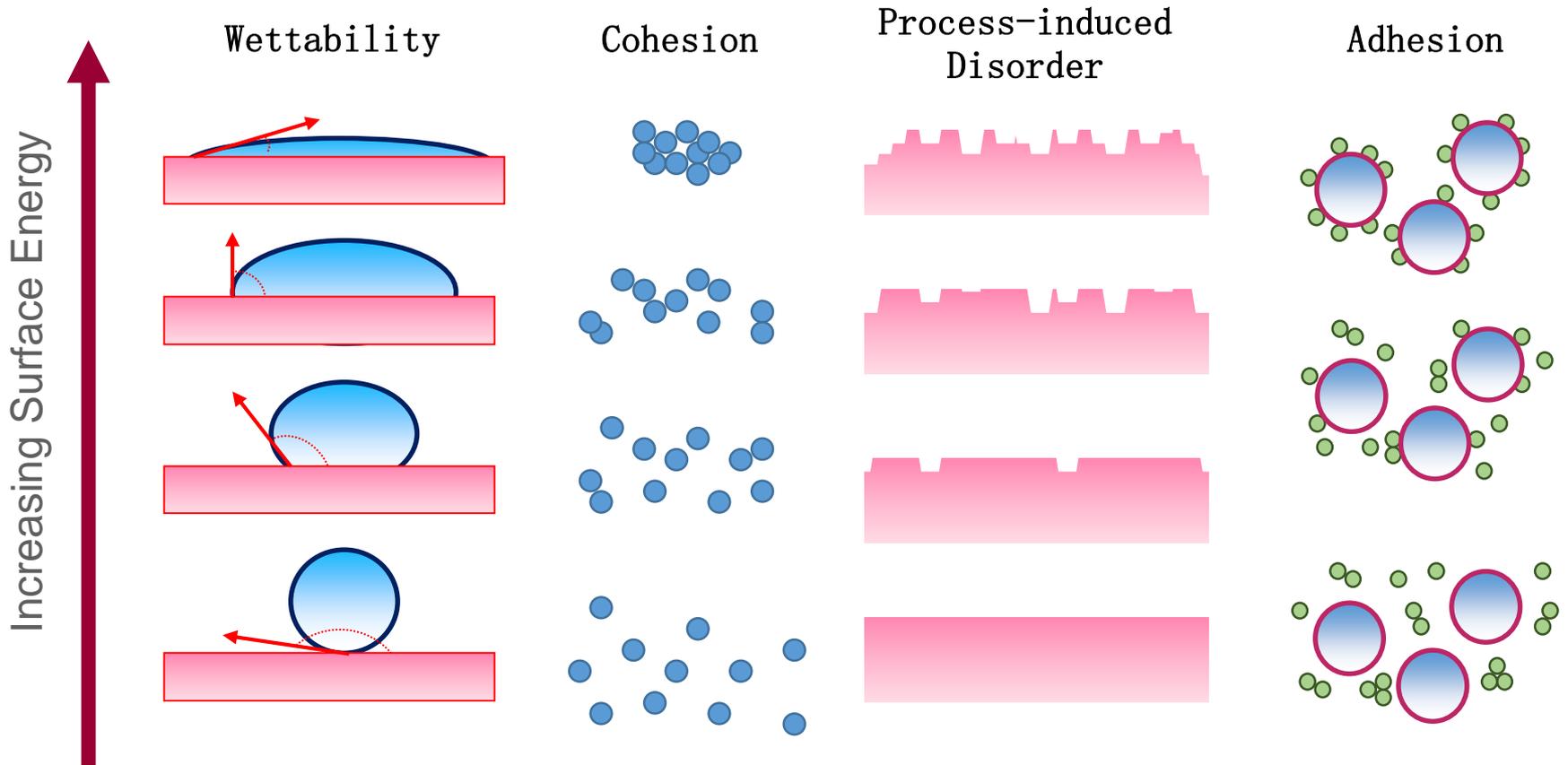
- metals' surface oxidation

Why it is important to measure?

Surface energy and its components between two interacting surfaces are critically important in a number of industrial applications including **adhesion, coating operations, printing, deinking, lubrication**; and has an influence in **daily life, biology, chemistry and biochemistry.**

Knowledge of surface energetics is important in the **formulation design** of multi-component systems and the prediction of **processing performance**.
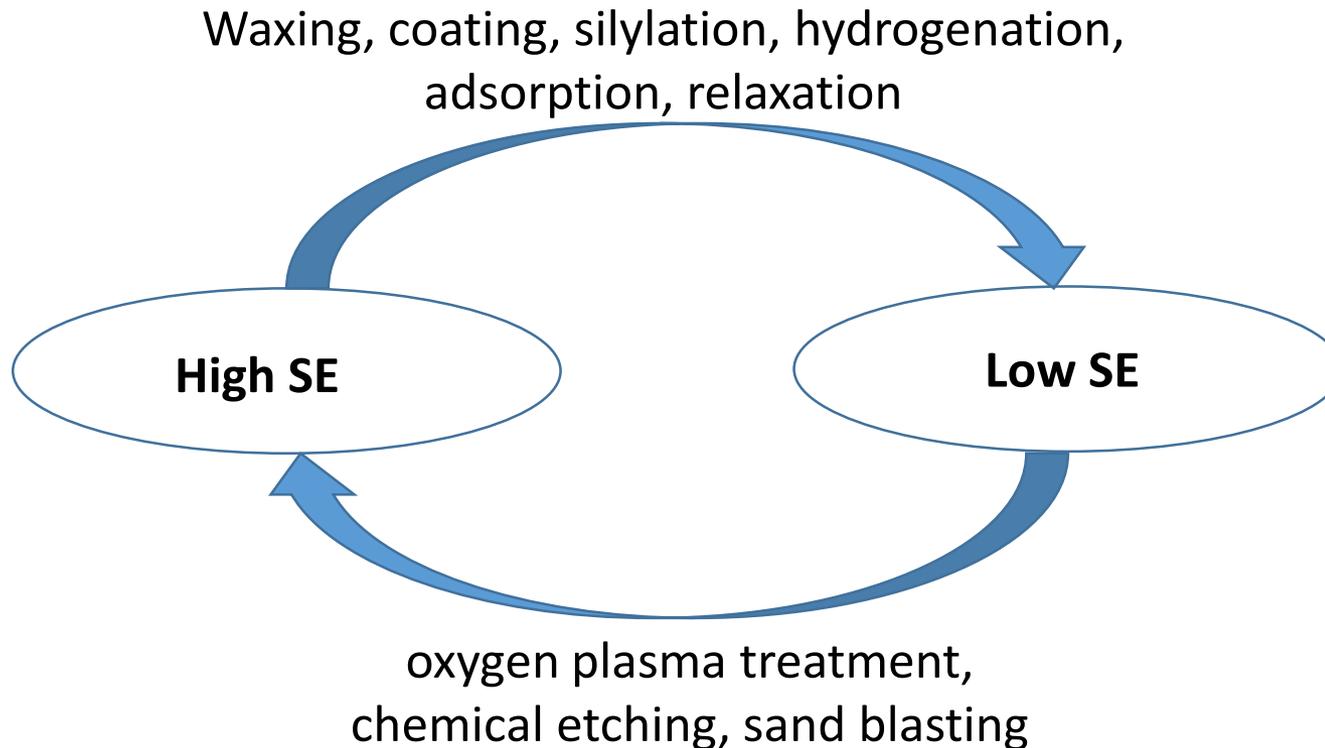
Thermodynamic parameters can be used to understand how solid surfaces interact :

- with each other → **cohesion**

- with vapours (e.g. moisture)

  sorption

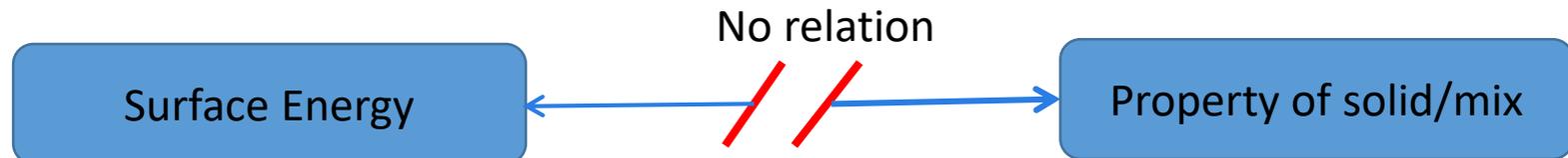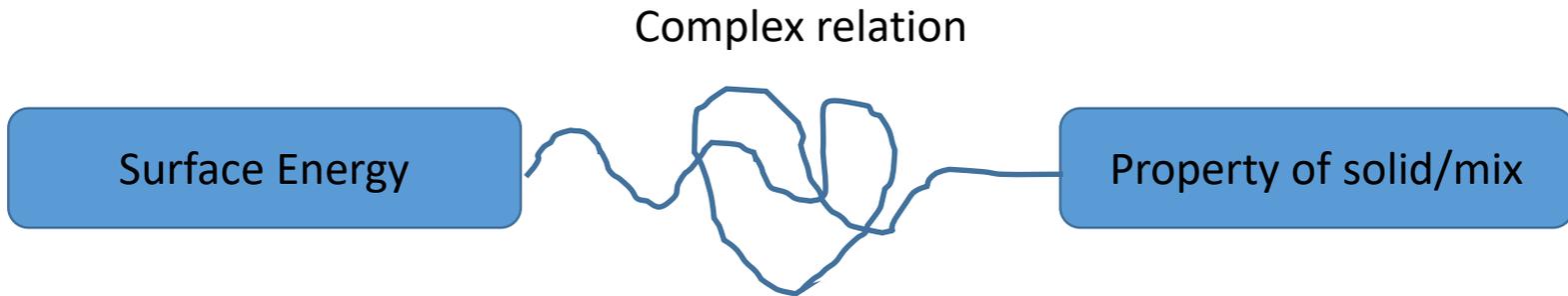- with liquids (e.g. solvents)

  wetting

- with other solid surfaces

  adhesion

Investigation the influence of the surface treatment

- Modifying surface energy of different materials at will

Waxing, coating, silylation, hydrogenation,
adsorption, relaxation

High SE → **Low SE**

oxygen plasma treatment,
chemical etching, sand blasting

BUT it is not correlate linearly with everything

| Surface Energy | ← Linear relation → | Property of solid/mix |

Complex relation

| Surface Energy | | Property of solid/mix |

No relation

| Surface Energy | ← // → | Property of solid/mix |
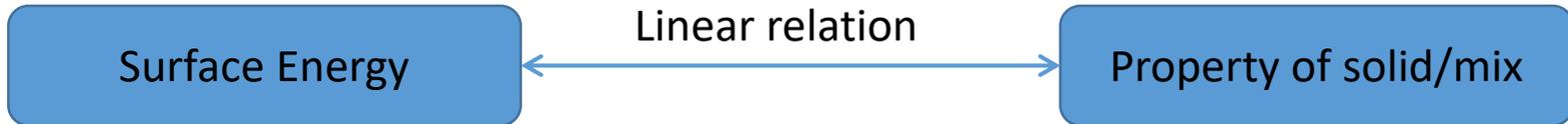
The property does not depends of the surface energy

Note: Does not mean that the surface energy value is wrong or not useful

- Contact Angle (CA) technique

- Atomic Force Microscope (AFM)

- Washburn capillary rise technique

- Inverse Gas Chromatography (IGC)

- Wetting Balance

If the surface energies of the individual compounds are known, the work of adhesion or cohesion can be obtained:

$$W_{Adh}^{total} = 2[(\gamma_1^d * \gamma_2^d)^{1/2} + (\gamma_1^+ * \gamma_2^-)^{1/2} + (\gamma_1^- * \gamma_2^+)^{1/2}]$$

$$W_{Coh}^{total} = 2[(\gamma_1^d * \gamma_1^d)^{1/2} + (\gamma_1^+ * \gamma_1^-)^{1/2} + (\gamma_1^- * \gamma_1^+)^{1/2}]$$

$$W^d \qquad\qquad W^{sp}$$

Work of cohesion - between *like* bodies

Work of adhesion - between *unlike* bodies
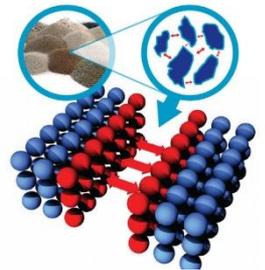
Higher W_{coh} value shows high tendency of aggregation in sample.

SEA Dispersive Surface Energy *Profiles*
- Correlation to SEA Heterogeneity Data

D-Mannitol	γ^D max	γ^D min	γ^D_{50}
Silanised	33.29	33.45	33.38
AR	37.51	52.63	40.34

SEA surface energy profile measurements
– ability to distinguish homogeneity and heterogeneity in surface free energy

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D-Mannitol	γ^{AB} max	γ^{AB} min	γ^{AB}_{50}
Silanised	1.54	1.59	1.57
AR	2.67	4.93	3.09
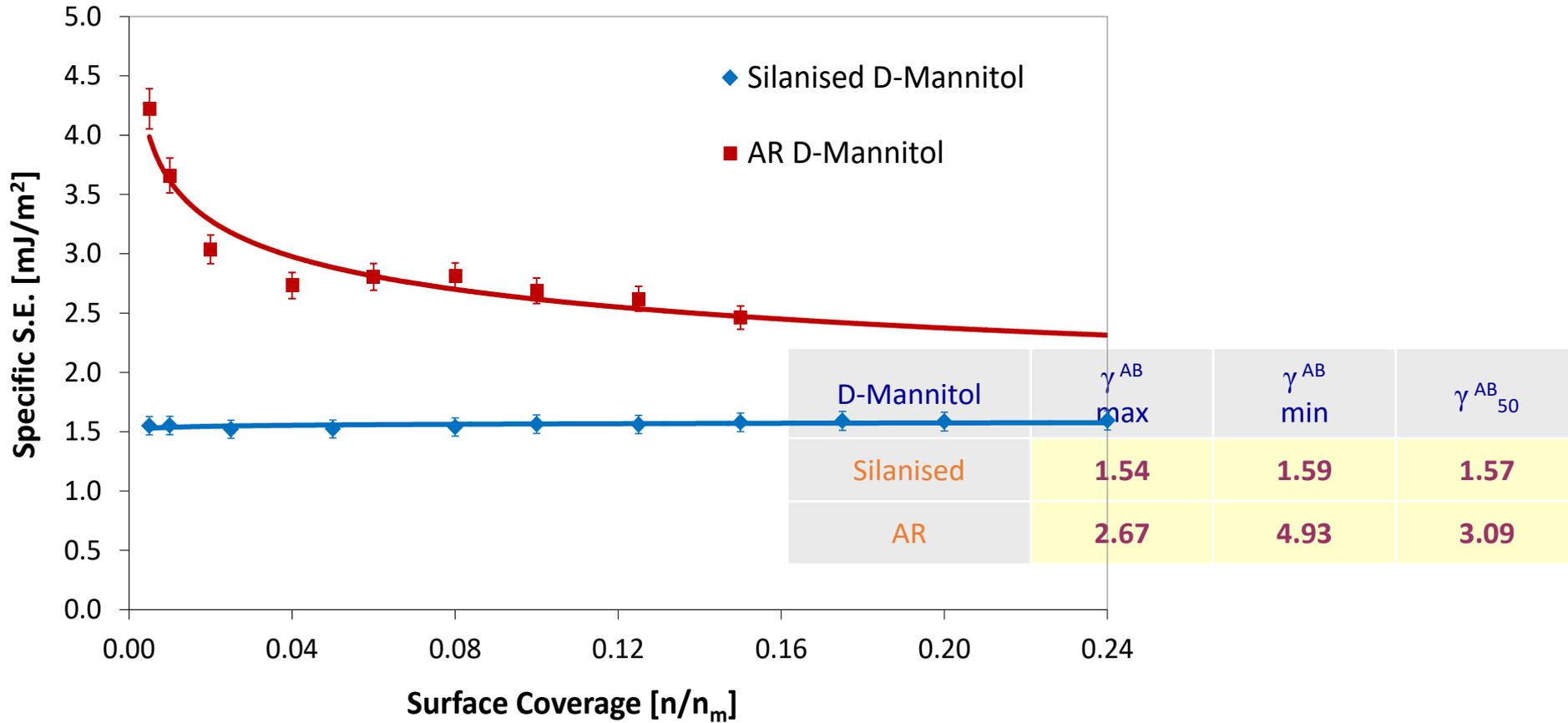
Changes in surface chemical environment - To an isotropic hydrophobic surface property

Work required to reversibly separate an interface between two bulk phases.

$$W_{Coh}^{total} = 2[(\gamma_s^D * \gamma_s^D)^{\frac{1}{2}} + (\gamma_s^+ * \gamma_s^-)^{\frac{1}{2}} + (\gamma_s^- * \gamma_s^+)^{\frac{1}{2}}]$$

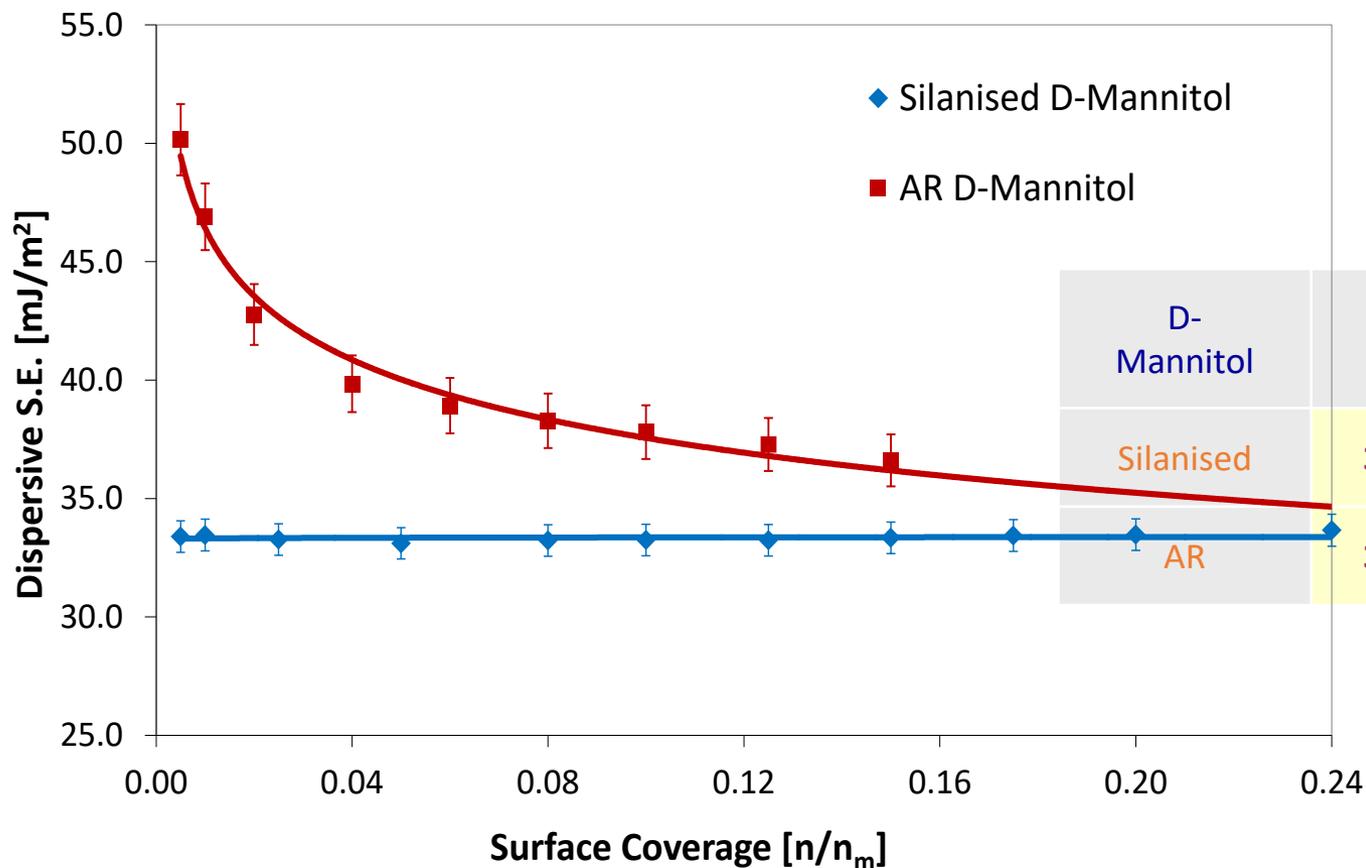# Surface Modification for Improved Flow Properties

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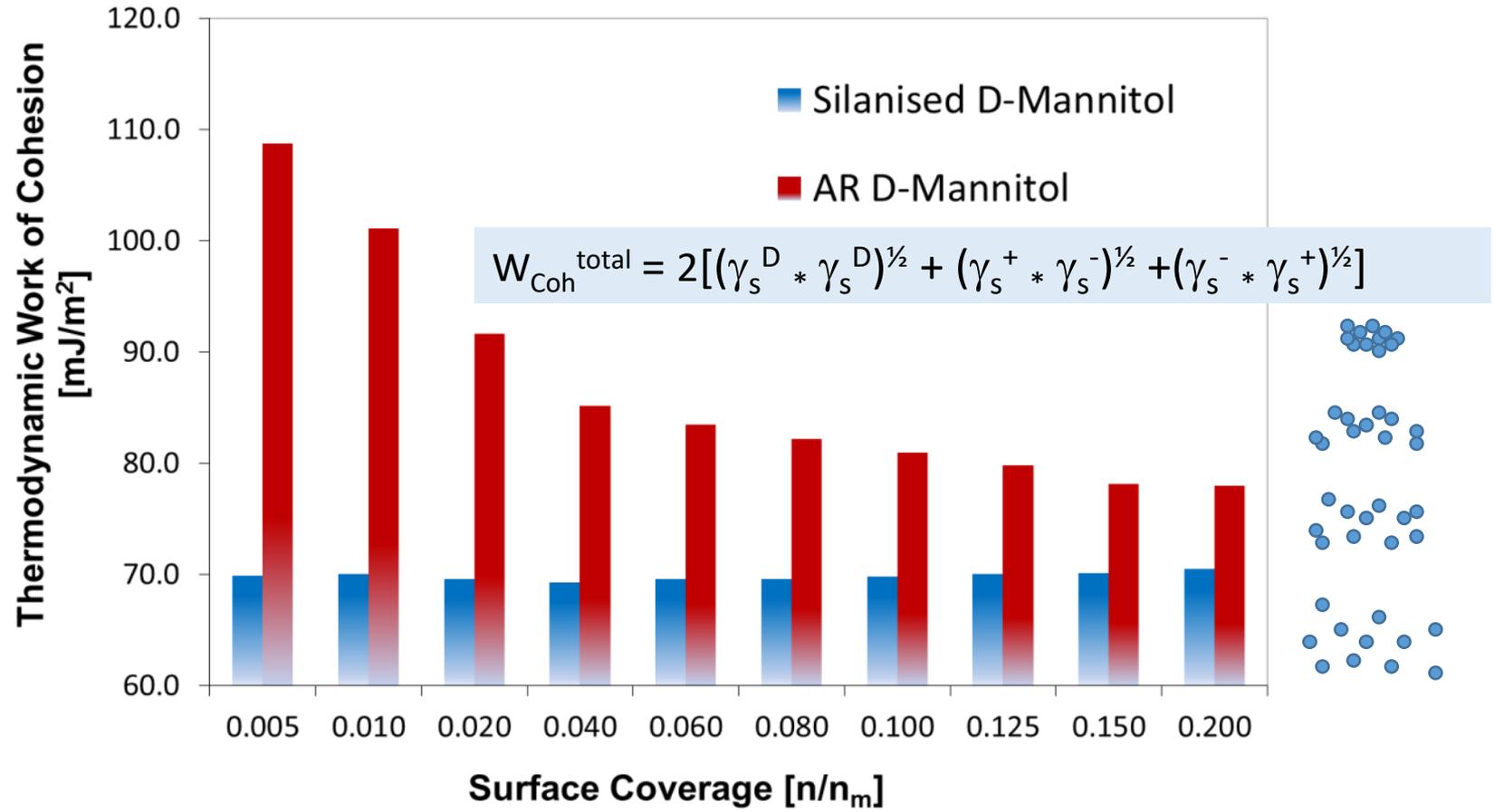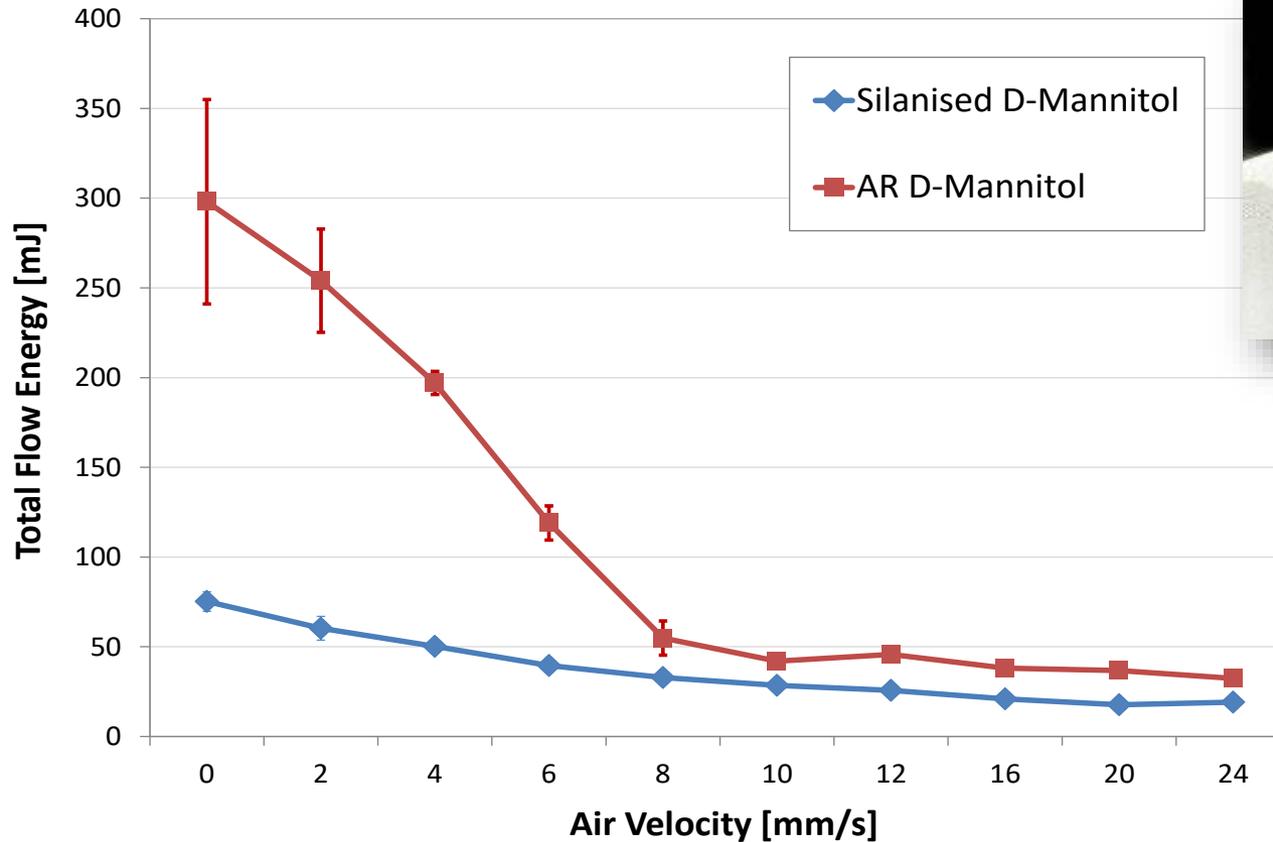
Free flowing materials fully aerate when flow energy stabilises

- Silanisation influences the dynamic flow properties, but not under consolidated conditions
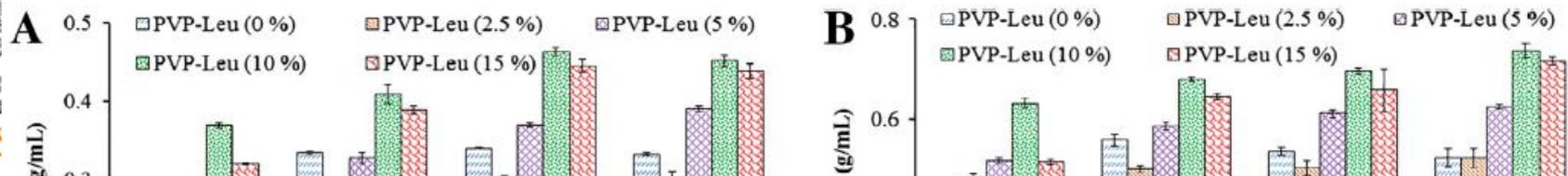
5. Conclusion

In conclusion, the surface energy derived cohesive–adhesive balance (CAB) model can effectively predict the interactive mixing behaviour of small particles. This data could also effectively predict the compactibility and flow behaviour of resultant interactive mixtures at certain excipient proportions. Overall, this knowledge may help provide significant insight into the mixing, flow and compaction behaviour of interactive mixture, and thus create optimum interactive powder mixtures for tablet manufacturing.
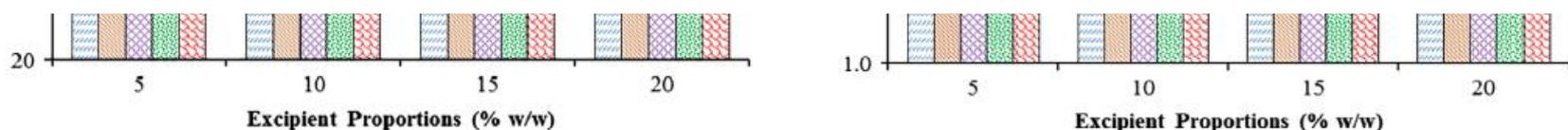
Fig. 4. Bulk density (A), tapped density (B), Carr's Index (C) and Hausner's ratio (D) data of API/excipient blends. Data represented as Mean ± SD ($n = 3$).

Materials

Drugs: Budesonide and Salbutamol sulphate

Excipient: α-Lactose-monohydrate

Formulation Tests

- Content Uniformity

Goal

- Use IGC to measure surface energetics of individual components (drugs and lactose)

- Using work of adhesion values calculated from IGC measurements to predict formulation performance

Surface Energy and Adhesion of DPI Compounds

Materials	γ^d (mJ/m^2)
Lactose	50.53
Budesonide	70.94
Salbutamol Sulphate	44.63
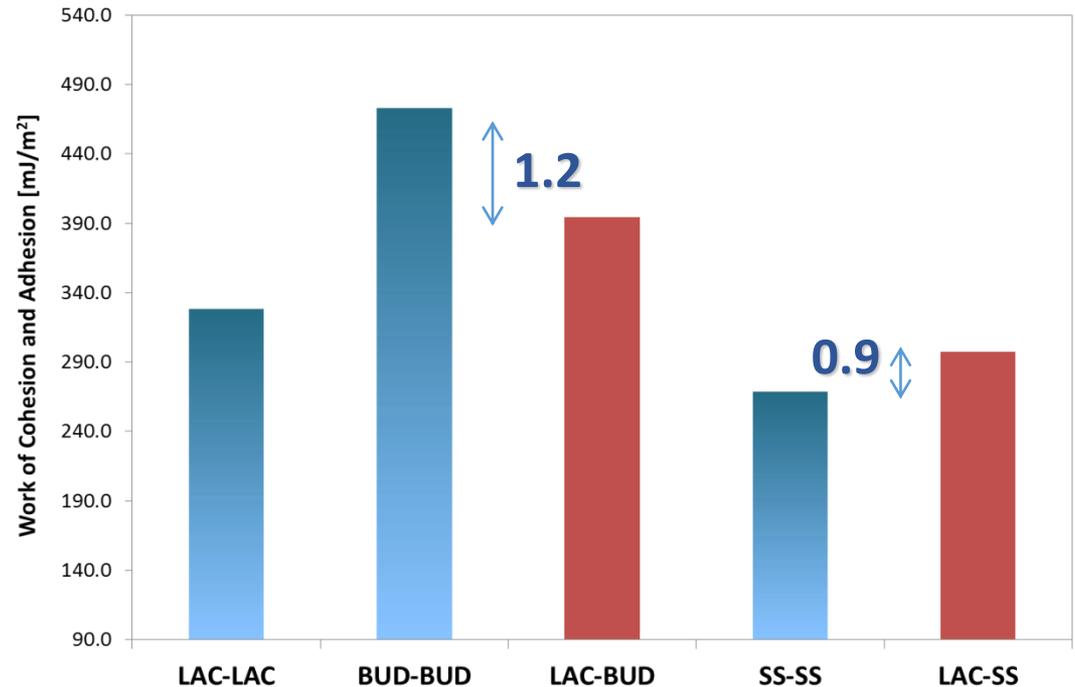
=>**Weak affinity** between Bud and Lac, poor blending performance expected

=>**Strong affinity** between SS and Lac, good blending performance expected
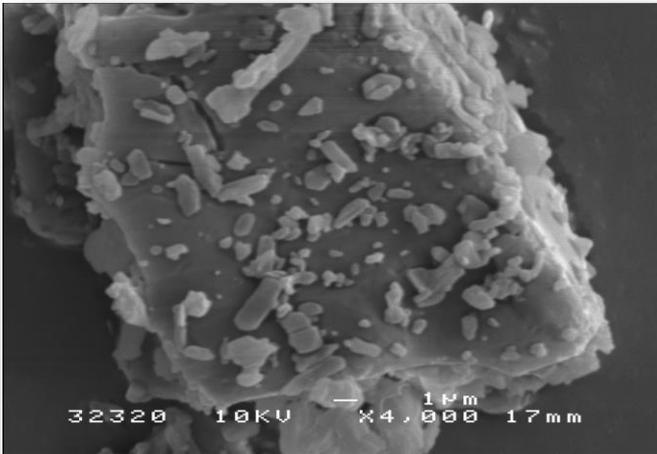
Salbutamol sulphate-Lactose

Budesonide-Lactose

Formulation	Content uniformity
	RSD (%)
Salbutamol+Lactose	4.2
Budesonide+Lactose	28.1

(Data by R. Price, Univ. of Bath, UK)

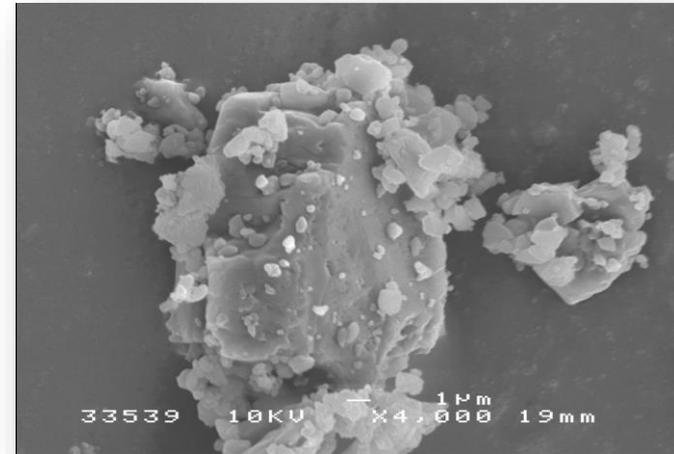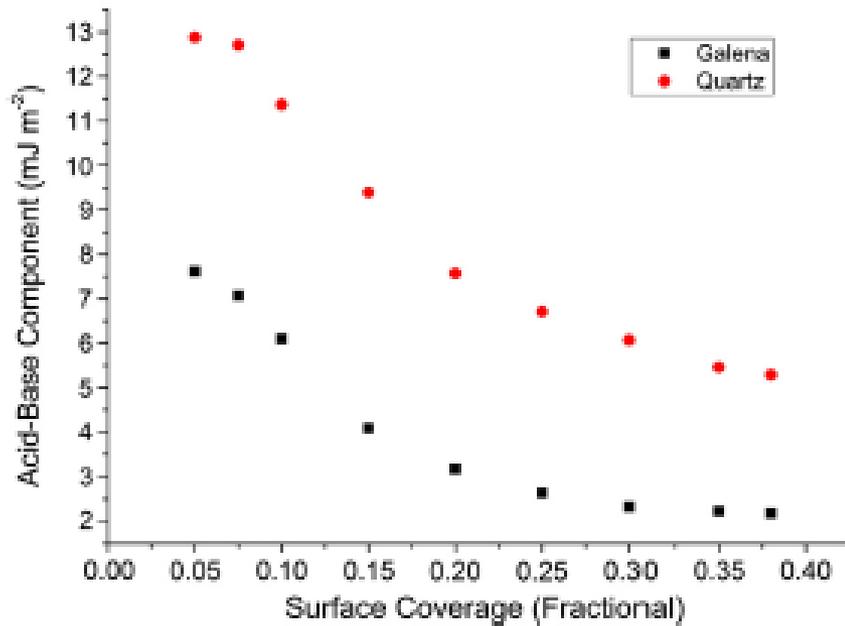**Quartz has higher acid-base/polar surface energy compared to Galena**
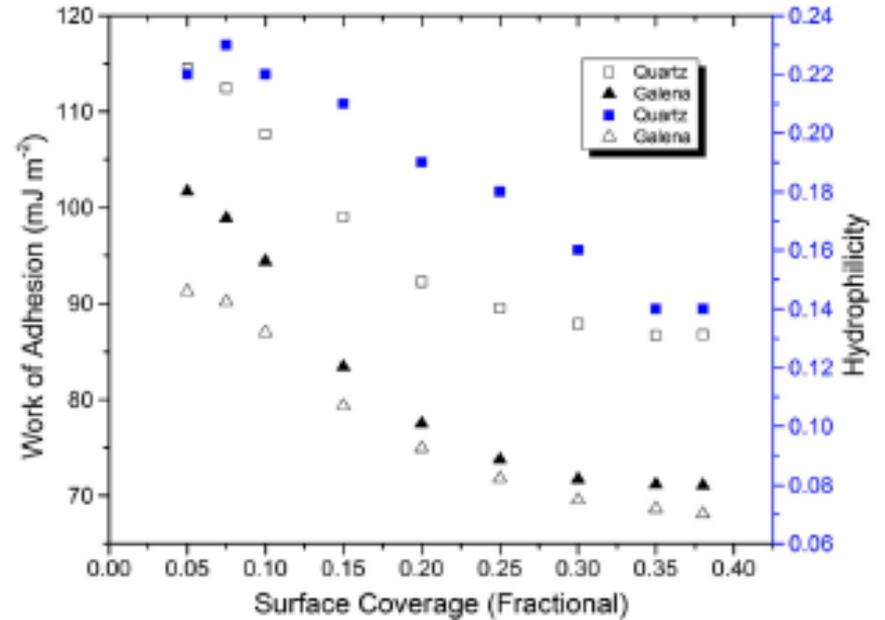
Quartz has surface hydrophilicity and work of adhesion to water

Mineral	Total mineral mass (g)	Average Recovery (%)	Standard deviation
Galena	1.00	27.63	1.05
Quartz	1.00	6.94	1.70

Higher hydrophilicity correlates to lower recovery during flotation

➢ **SSM Ali, JYY Heng, AA Nikolaev, and KE Waters., Powder Technology *249* (2013) 373-377.**

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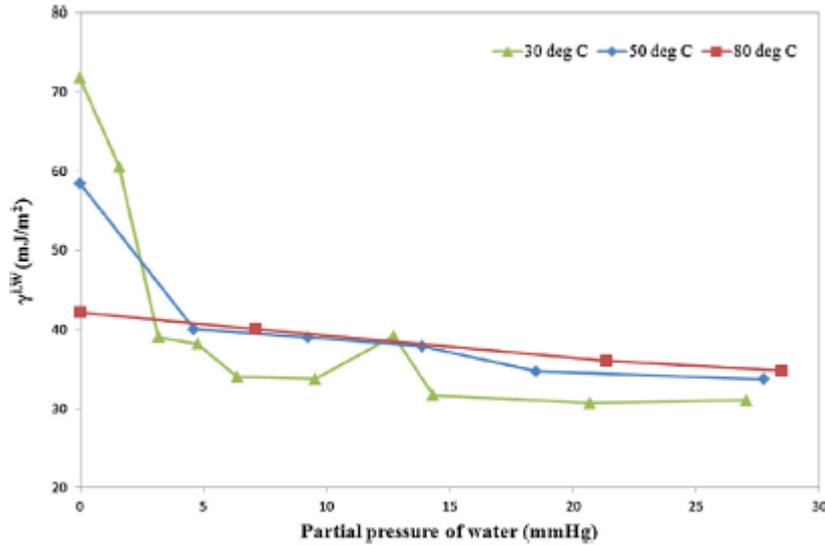
Dispersive SE as a function of water vapor pressure for calcite
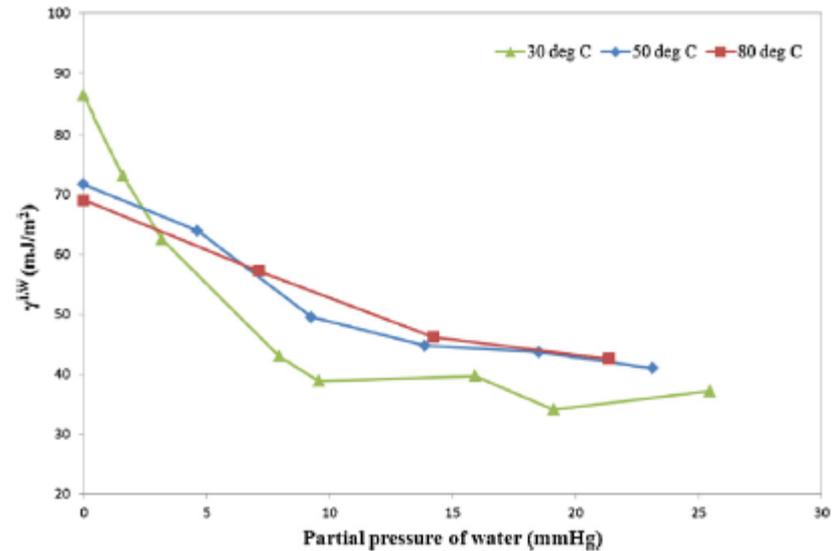
Dispersive SE as a function of water vapor pressure for dolomite

Higher water vapor contents lead to decrease in dispersive surface energy
Dolomite had higher dispersive surface energy
Surface energy related to reservoir rock wetting

➤ N Arsalan, SS Palayangoda, DJ Burnett, JJ Buiting, and QP Nguyen., Colloids and Surfaces A *436* (2013) 139-147.

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To predict nanofiller-polyurethane composite mechanical performance

- **Carbon Nanotubes**

  - As received (**AR-MWNT**)

  - Oxidised with HNO_3 solution to create -COOH functional groups (**MWNT-COOH**)

- **Nanoclay**

  - As received (**AR-nanoclay**)

  - Surface treated with isophrone diisocyanate - isocyanate functional groups (**fNCO-nanoclay**)

- **Polyurethane Matrix** (**PU**)

Adhesion between matrix resin and carbon fiber is crucial in a reinforced composite; during the manufacture of carbon fiber, surface treatment is performed to enhance this adhesion.

Collaboration with National Institute of Standards and Technology (**NIST**), Gaithersburg, US.

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- With a higher surface energy, the greater cohesive forces between the AR-Nanoclay particles, and between MWNT-COOH particles

- Particle-particle interactions dominate thermodynamically, leading to poor dispersion and decreased load transfer

Adhesion/Cohesion Balance
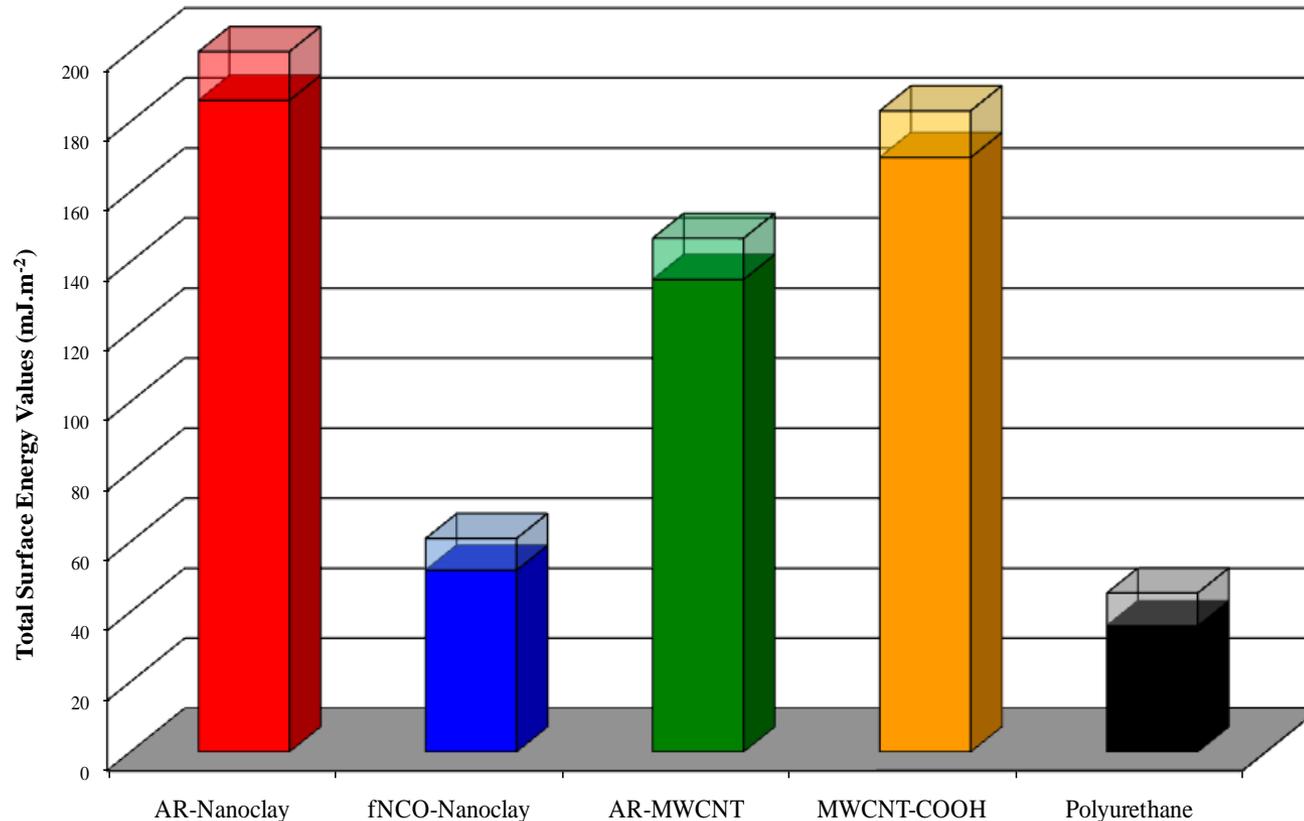
Thermodynamic works of adhesion cohesion values for the nanofiller/PU composites

Sample	$W_{adhesion}$ [mJ/m²]	$W_{cohesion}$ [mJ/m²]	W_{ad} / W_{coh}
AR-MWNT	160.4	293.4	0.55
MWNT-COOH	178.8	366.2	0.49
AR-nanoclay	188.3	404.3	0.47
fNCO-nanoclay	104.9	121.9	0.86

- W_{ad}/W_{coh} ratio -- indication of the balance of forces between adhesion and cohesion.
- Too strong or too weak particle-particle interactions, increased segregation of the particles or poor dispersion, resulting in decreased particle-matrix interactions.
- Ideally, formulations should be developed to optimize the W_{ad}/W_{coh} ratio.

Mechanical Performances

Sample	Tensile Modulus [GPa]	Tensile Strength at Break [MPa]	Tg (°C) [max tan δ]
PU alone	1.46 ± 0.13	61 ± 4	81
0.5% AR-MWNT	1.93 ± 0.17	60 ± 7	79
0.5% MWNT-COOH	1.53 ± 0.14	56 ± 6	76.5
1.0% AR-nanoclay	2.05 ± 0.15	54 ± 11	77.5
1.0% fNCO-nanoclay	2.31 ± 0.12	71 ± 7	80.8

- AR-MWNT composite and fNCO-nanoclay have superior mechanical properties (tensile strength and modulus) and higher W_{ad}/W_{coh} ratios.

*A. Granier et al., Adhesion Soc. Annual Meeting Pro., 2007.

- Solid dosage form accounts for more than 70% of all drug administration.

- Granulation is extensively used in other industries such as food, catalyst, agrichemicals and minerals.

- The annual value of all granular products in trillions of US dollars.

- But............ '*More of an art than science*' (Iveson et al. 2001).
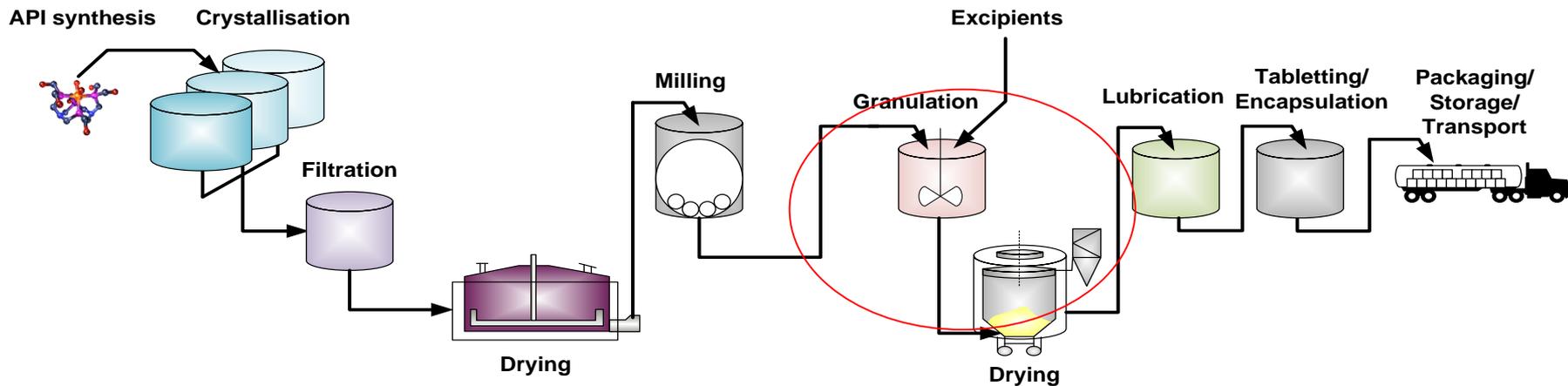
S. M. Iveson, J. D. Litster, K. Hapgood, and B. J. Ennis. Powder Technology 117: 3-39 (2001).

- Granulation typically involves the co-agglomeration of small crystals of API with excipient (with or without liquid binder).

- Granulation done typically to improve powder flow, compaction, and composition uniformity.

- Granulation behavior can be sensitive to properties of the primary solid particles.
  - Particle morphology, density and size distribution
  - Surface energy or wetting characteristics

- Poor wetting can lead to weak, porous granules and inadequate binder distribution

- The surface energy of the solid particles will determine the ability of binder solution to spread across the surface of the particles.

- Selection of the correct binder and wetting agent in a granulation process can critically determine the performance and stability of the resultant granules and product.

- These solid-binder interactions will also influence the strength of adhesion of the solids to the dry binder, thus determining the mechanical performance of the final agglomerates or product.

- ## Materials
    - Compound A with low bulk density (0.12 g/cm^3)
    - Solvents: Water and 20 vol. % EtOH in water
- ## Granule Properties
    - Density, Porosity, and Friability
- ## Goal
    - Use surface energy values to determine spreading coefficients (binder over drug) and predict granule properties
    - D. Zhang, J.H. Flory, S. Panmai, U. Batra, and M.J. Kaufman, Colloids and Surfaces A., 206 (2002) 547-554.

Material	Surface Energy (mJ/m^2)	γ^d	γ^p	Spreading Coefficient (λ)
Water	72.1	19.9	52.3	-94
20% EtOH in Water	38.5	14.6	23.9	-30
Drug A	34.8	34.7	0.1	-

$$\lambda_{1/2} = 4 \left[\frac{\gamma_1^D \gamma_2^D}{\gamma_1^D + \gamma_2^D} + \frac{\gamma_1^{SP} \gamma_2^{SP}}{\gamma_1^{SP} + \gamma_2^{SP}} - \frac{\gamma_1^T}{2} \right]$$

- Liquid surface tensions taken from literature, Drug A surface energy measured by contact angle on compacted powder

Solvent	Loose Density (g/cm^3)	Tapped Density (g/cm^3)	Porosity	Friability
None	0.12	0.21	-	-
Water	0.26	0.37	34%	30%
20% EtOH in water	0.32	0.44	20%	5%

- Higher wettability of 20% EtOH solution lead to lower porosity (deeper solvent penetration)
- Higher wettability of 20% EtOH solution lead to stronger granules (higher density and lower friability)

- ## Materials
  - API: Ibuprofen and Naporxen
  - Binder: HPC, HPMC, and PVP
- ## Tablet Properties
  - Tablet Hardness and Tablet Friability
- ## Goal
  - Use wetting studies (Washburn experiments) to determine API surface energy via Zisman plots and predict granule properties
- K.M. Lusvardi, T. Durig, G.W. Skinner, and W.W. Harcum, Hercules Incorporated, Pharmaceutical Technology Report, PTR-026.
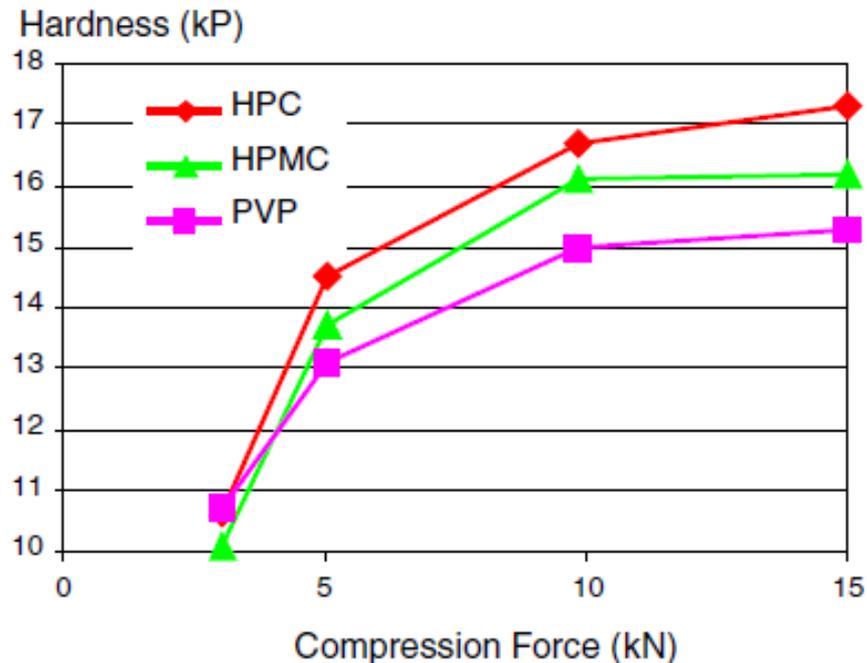
Ibuprofen Wetting Behavior

Wetting Solution	Surface Tension (mJ/m^2)	Viscosity (cP)	Contact Angle
N-Hexane	18.4	0.3	0
HPC	40.0	2.3	68
HPMC	48.4	1.9	81
PVP	53.6	1.5	88
Water	72.1	1.0	No wetting, >90

- HPC shows strongest wetting behavior (lowest contact angle); extrapolated solid surface energy ~19 mJ/m^2
- High contact angles indicate poor wetting: poor drug-binder interactions

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Ibuprofen Tablet Behavior

Effects of 4 Wt % Binders on Ibuprofen Tablet Hardness

- HPC shows stronger tablet performance
- Overall low tablet strength

Naproxen Wetting Behavior

Wetting Solution	Surface Tension (mJ/m^2)	Viscosity (cP)	Contact Angle
N-Hexane	18.4	0.3	0
HPC	40.0	2.3	0
HPMC	48.4	1.9	37
PVP	53.6	1.5	63
Water	72.1	1.0	85

- HPC shows strongest wetting behavior (lowest contact angle); extrapolated solid surface energy ~40 mJ/m^2
- Low contact angles indicate good wetting: stronger drug-binder interactions

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Naproxen Tablet Behavior

Effects of 4 Wt % Binders on Naproxen Tablet Hardness
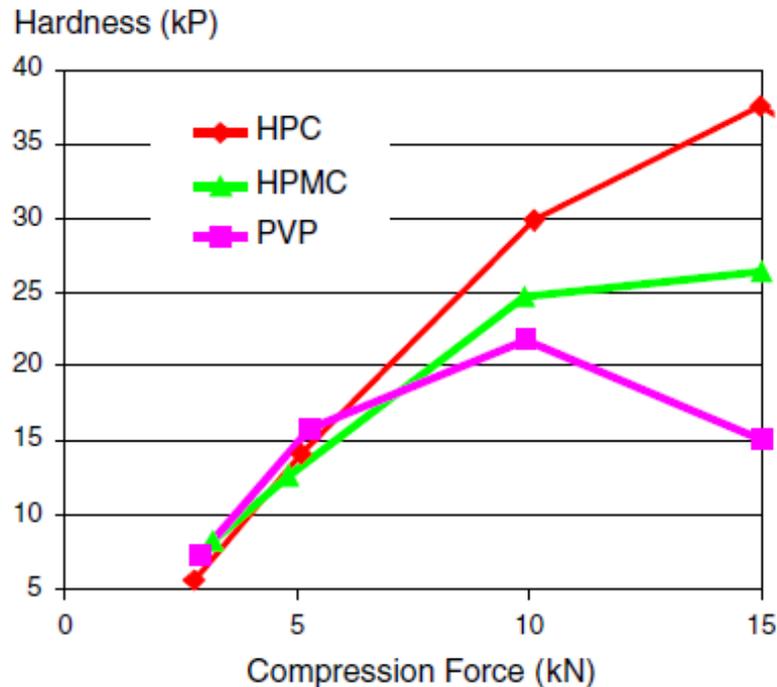
- HPC shows stronger tablet performance; stronger tablets than Ibuprofen
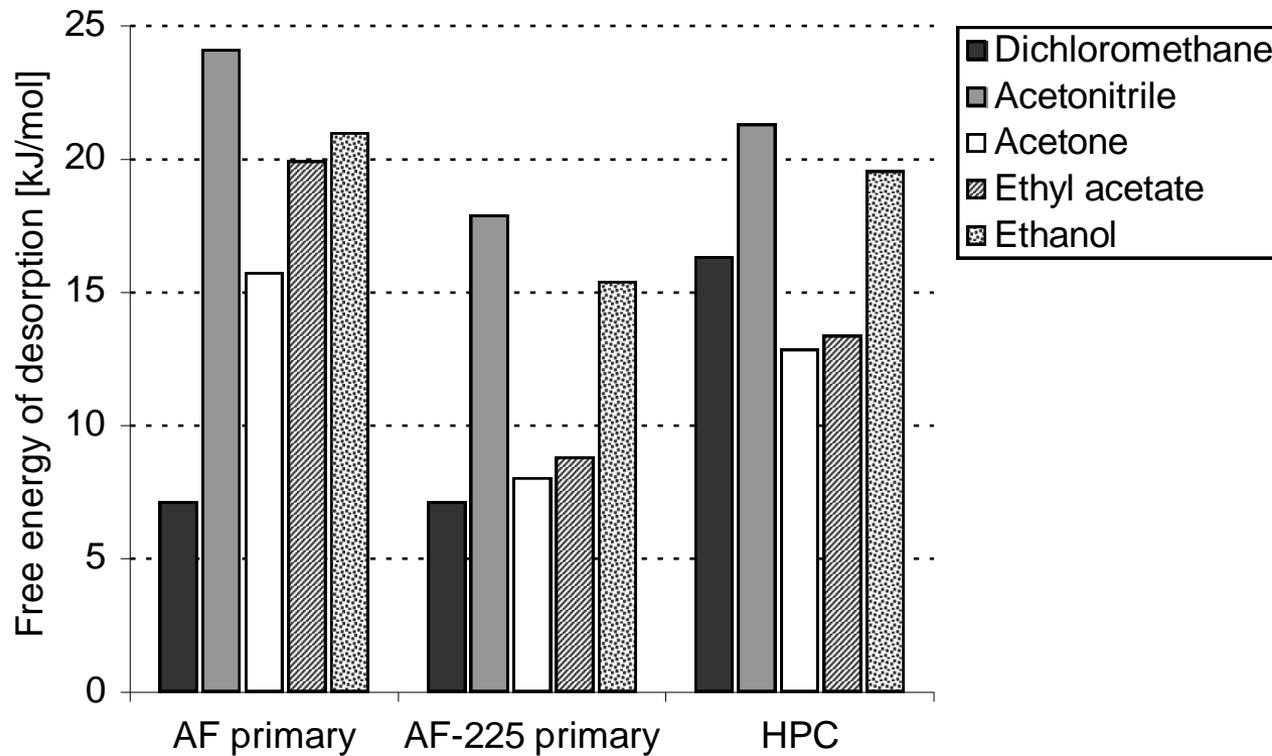- Wetting and surface energy data correlate with tablet strength

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- ## Materials
  - Model "Active": Hydrophilic and hydrophobic glass beads of two different particle sizes
  - Binders: Hydroxypropylcellulose (HPC)
- ## Granule Properties
  - Fluidized bed granulation
  - Particle size distribution measurements and Imaging
- ## Goal
  - Use IGC to measure surface energetics of individual components (drugs and binders) and correlate to granulation behaviour

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- **Hydrophilic glass beads show higher disp. surface energies than hydrophobic**
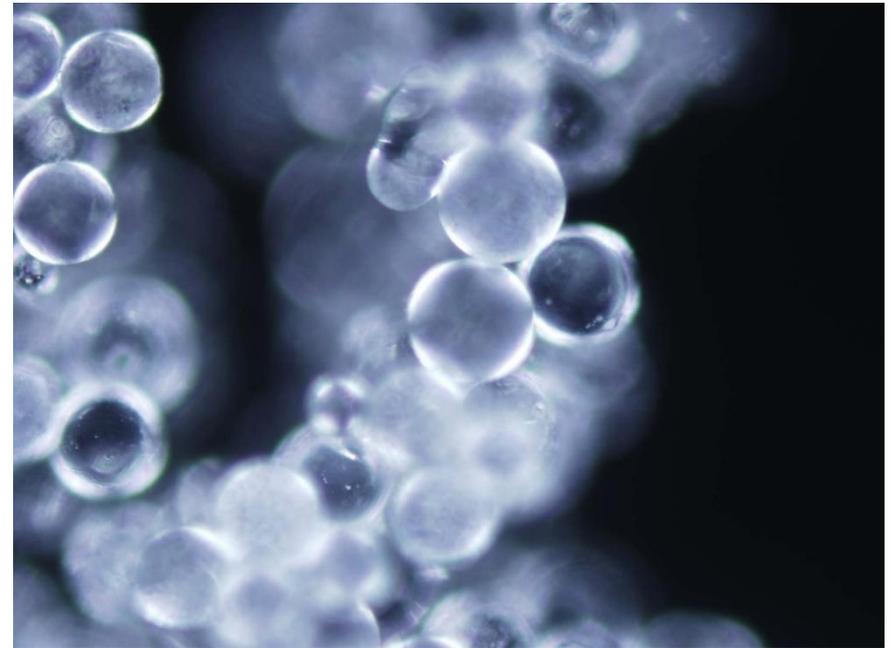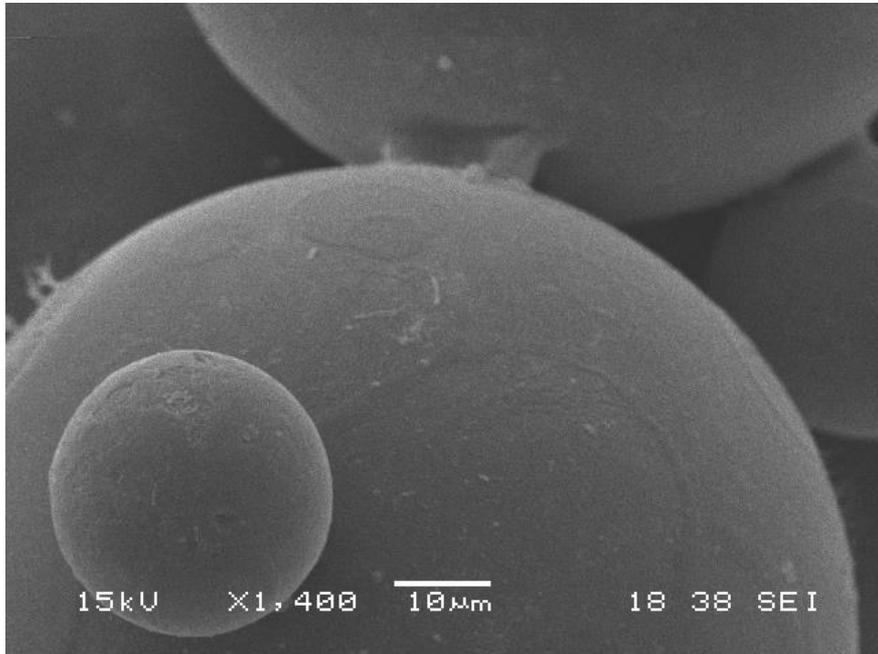- **Particle size has no impact on the results**

Figure 1: Dispersive component of the surface energy for the samples

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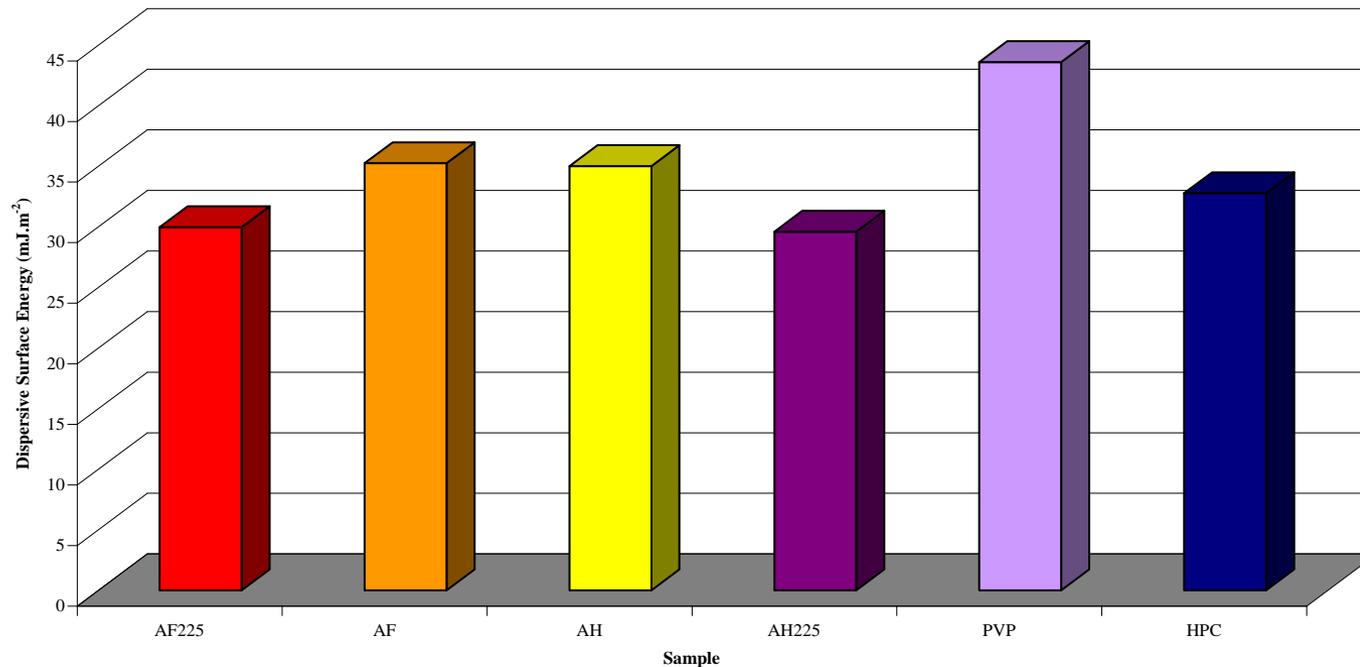
• **Specific free energies show "fingerprint" of beads and binder**

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- **Granules from hydrophilic beads**

Contact angle of binder solution: 0' (complete wetting)

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- **Granules from hydrophobic beads**

Contact angle of binder solution: 114+/-6'

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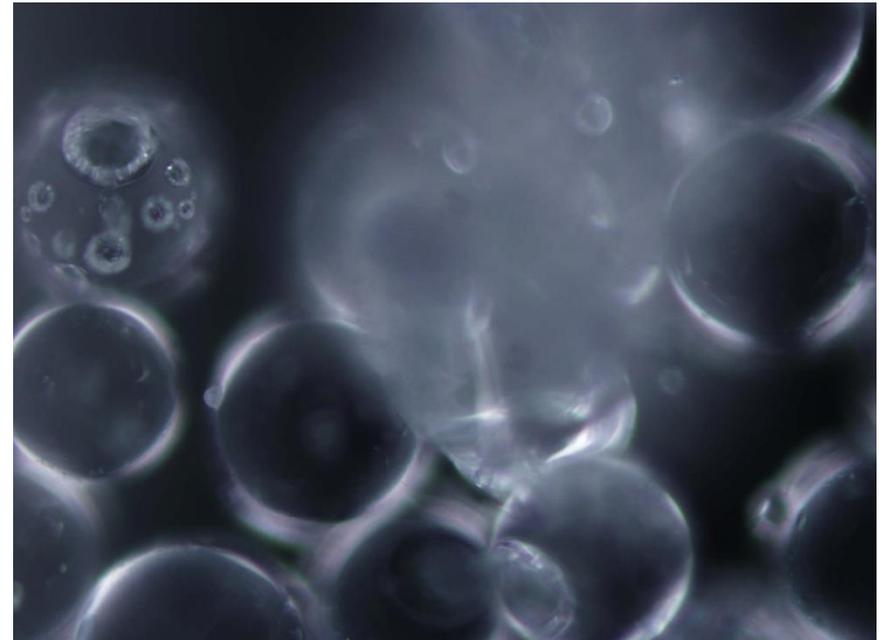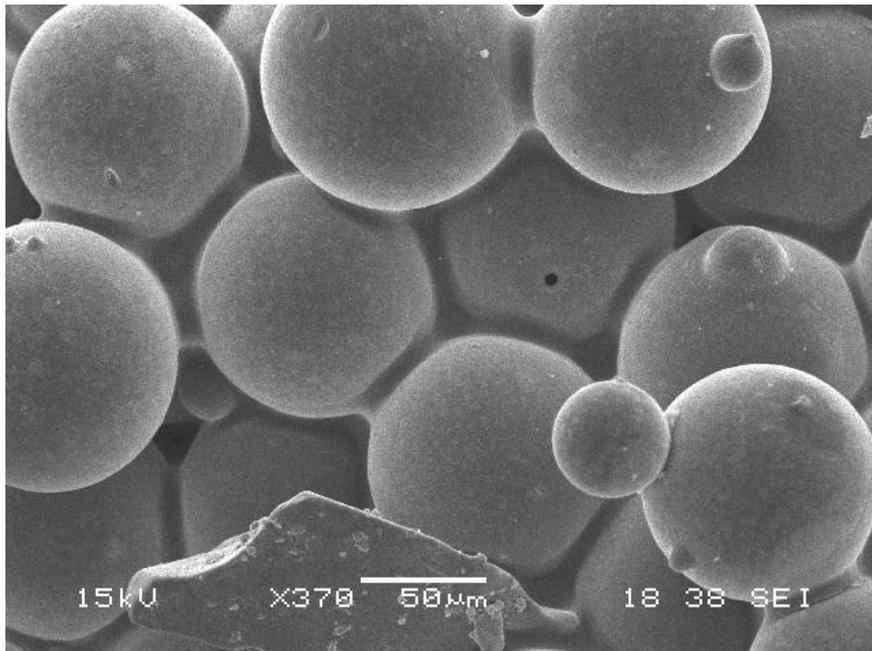
hydrophilic

hydrophobic

Particle size distribution

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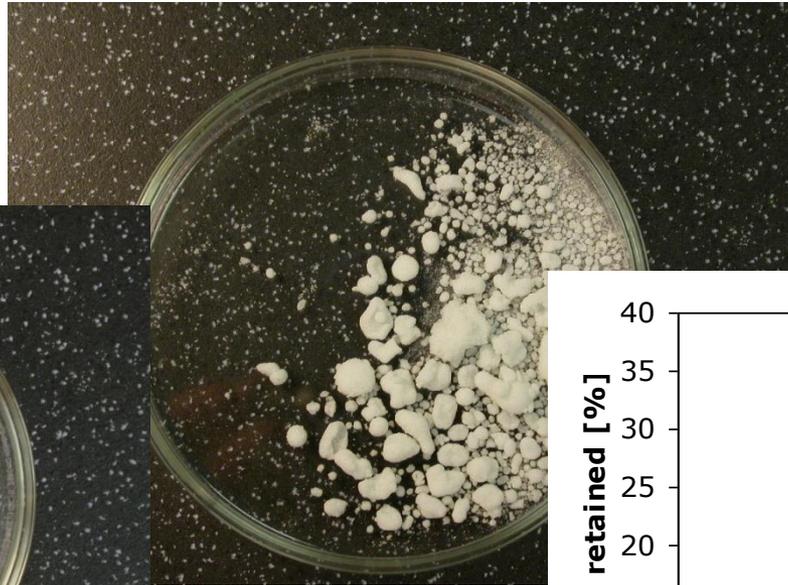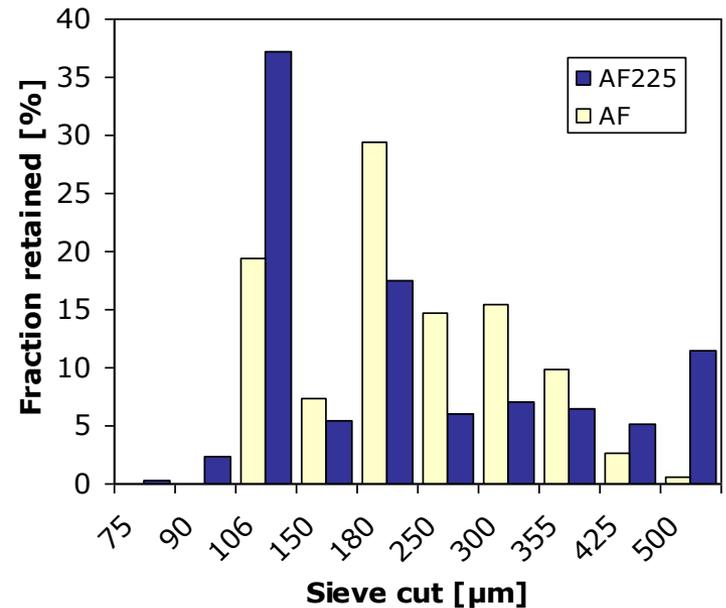
- **Hydrophilic granules show finger print of HPC**
- **Hydrophobic granules a mixture of HPC and beads**
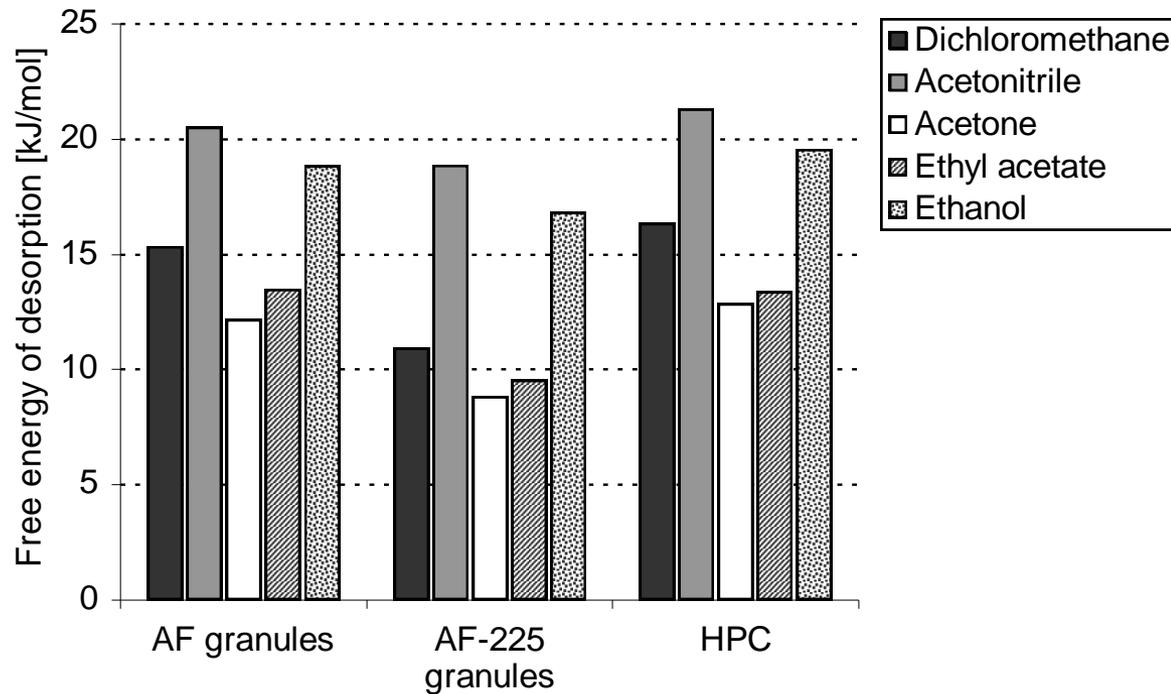
Results

- Binder appears to "spread" on hydrophilic glass beads which results in "coating".
- Hydrophobic glass beads show "islands" of binder and solid bridges can be formed.
- Due to spreading of binder little granulation occurs with hydrophilic glass beads and mean particle size is rather small.
- Hydrophobic glass beads show bigger granules as solid bridges can be formed although size distribution is wide due to non-optimised granulation conditions.

- **Surface energy is an important particle property**

- **Surface energy can be related to powder cohesion and powder flow**

- **Cohesion/Adhesion balance can help predict composite performance**

- **Surface energy is related to wetting behavior of binders and granule size/strength**

- **Surface Measurement Systems Scientists, current and former: Frank Thielmann, Raimundo Ho, Majid Naderi, Manaswini Acharya, Anett Kondor, Armando Garcia**

- **Dr. Jerry YY Heng and Surfaces and Particle Engineering Lab; London Imperial College**

- **IFPRI Workshop organizers**

- **Time and Attention**