

Dry Coating Forum 2025



Influence of materials properties and process parameters on particle arrangement for dry LIB electrodes

Alex Lemarinel^{1,2}, Maria Graciela Cares¹, Jesus Alberto Barreras Uruchurtu², Clément Paul³, Thomas Philippe², Véronique Falk¹

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(1) University of Lorraine, CNRS, LRGP, F-54000 Nancy, France

(2) Ampère (Renault Group), Lardy, France

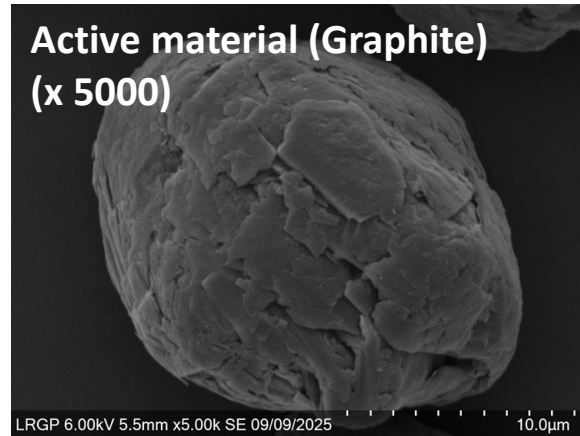
(3) Arkema, Serquigny, France



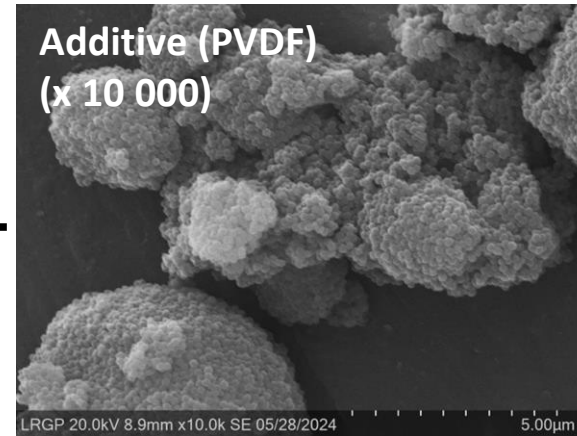
- Cheaper electrode
- Safer process
- High-performance electrode



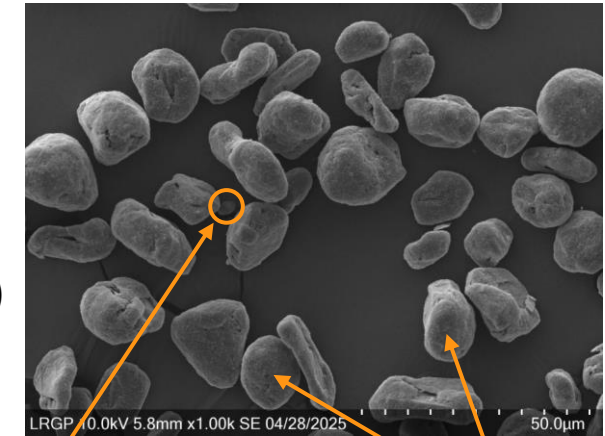
Dry mixing of electrode materials



+



Dry mixing step
→
(High shear mixer)



PVDF aggregate

Graphite particles covered by
PVDF unit particles

- Particle coating is investigated in particle technology :

Food



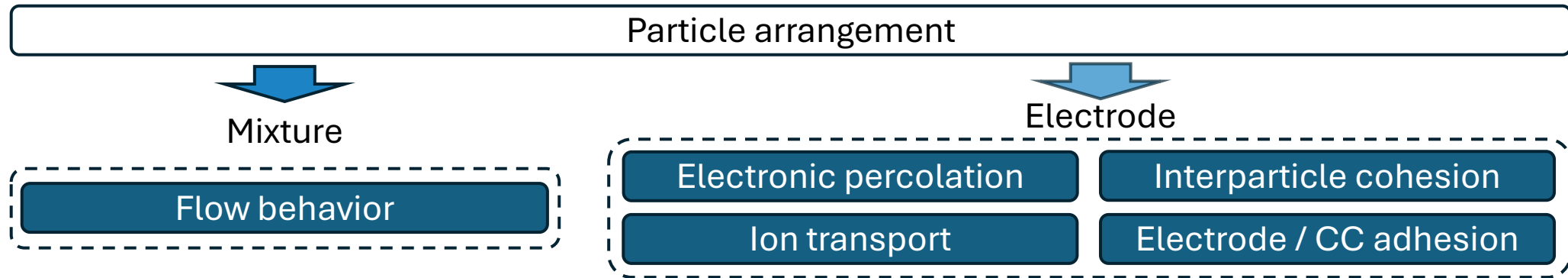
Health



Cosmetics



- Surface modification → powder properties (flowability, compressibility, ...)



How powders properties and mixing parameters influence particle arrangement during mixing ?

I – Materials and methods

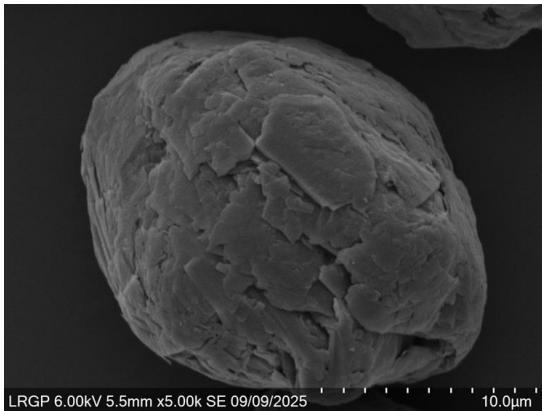
II – Mixing step study : key materials characteristics

III – Powder surface energy & surface coverage: aptitude to interact

IV – Conclusion and perspectives

Active material

Graphite (Gr)



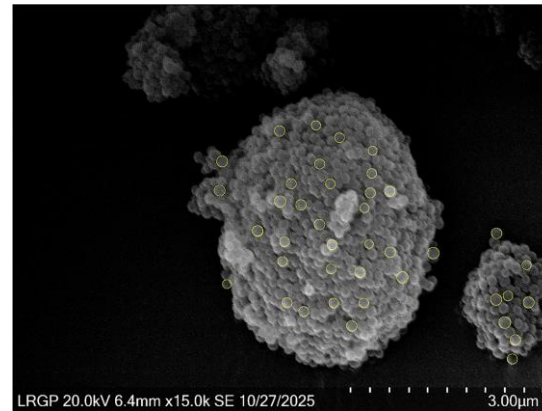
$D[3,2]$: Diameter of a sphere
with same volume/surface ratio

$$D[3,2]_{Gr} = 14.3 \mu\text{m}$$

(laser granulometry)

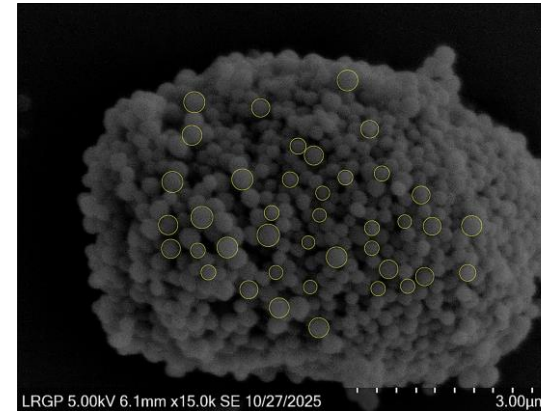
Binder

PVDF-1



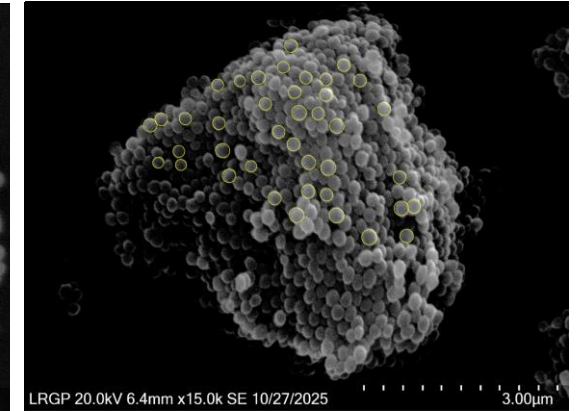
$$D_{50} = 160 \pm 20 \text{ nm}$$

PVDF-2



$$D_{50} = 270 \pm 40 \text{ nm}$$

PVDF-3



$$D_{50} = 200 \pm 20 \text{ nm}$$

D_{50} : Median diameter of a sphere with equivalent surface

(SEM micrographs)

I – Mixing step

- Lab scale high-shear mixer : ProCepT Mi-Pro
 - $V = 500 \text{ mL}$
 - $d_{\text{bowl}} = 10 \text{ cm}$
 - Mixing intensity : 3000 rpm

- Mixing parameters :

Mixing time :

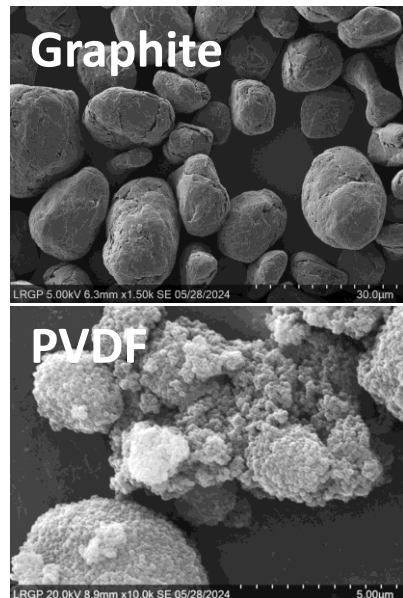
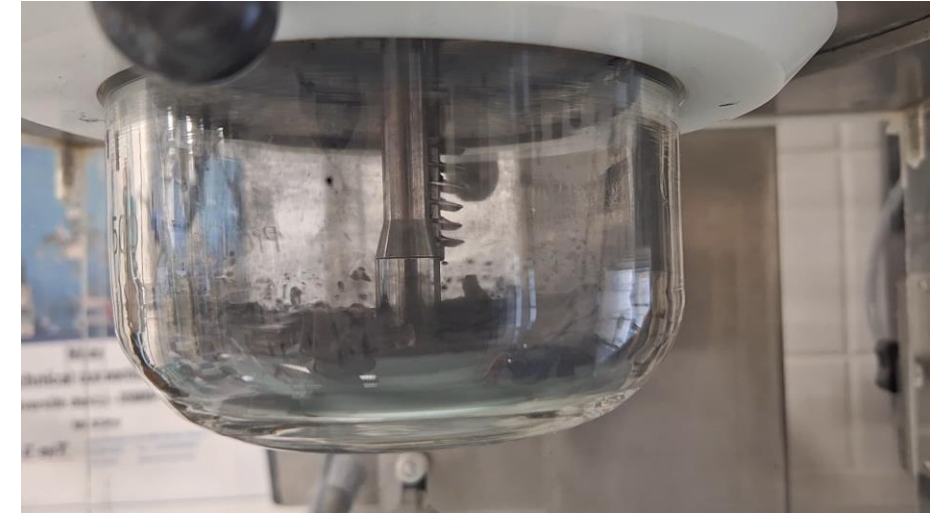
- $30\text{s} \rightarrow 900\text{s}$

Binder nature :

- PVDF-1
- PVDF-2
- PVDF-3

PVDF-1 %wt :

- 0.5 %wt
- 1% wt
- 2% wt



homogenization
(spatula)



High-shear
mixing
(3000 rpm)



I – Materials and methods

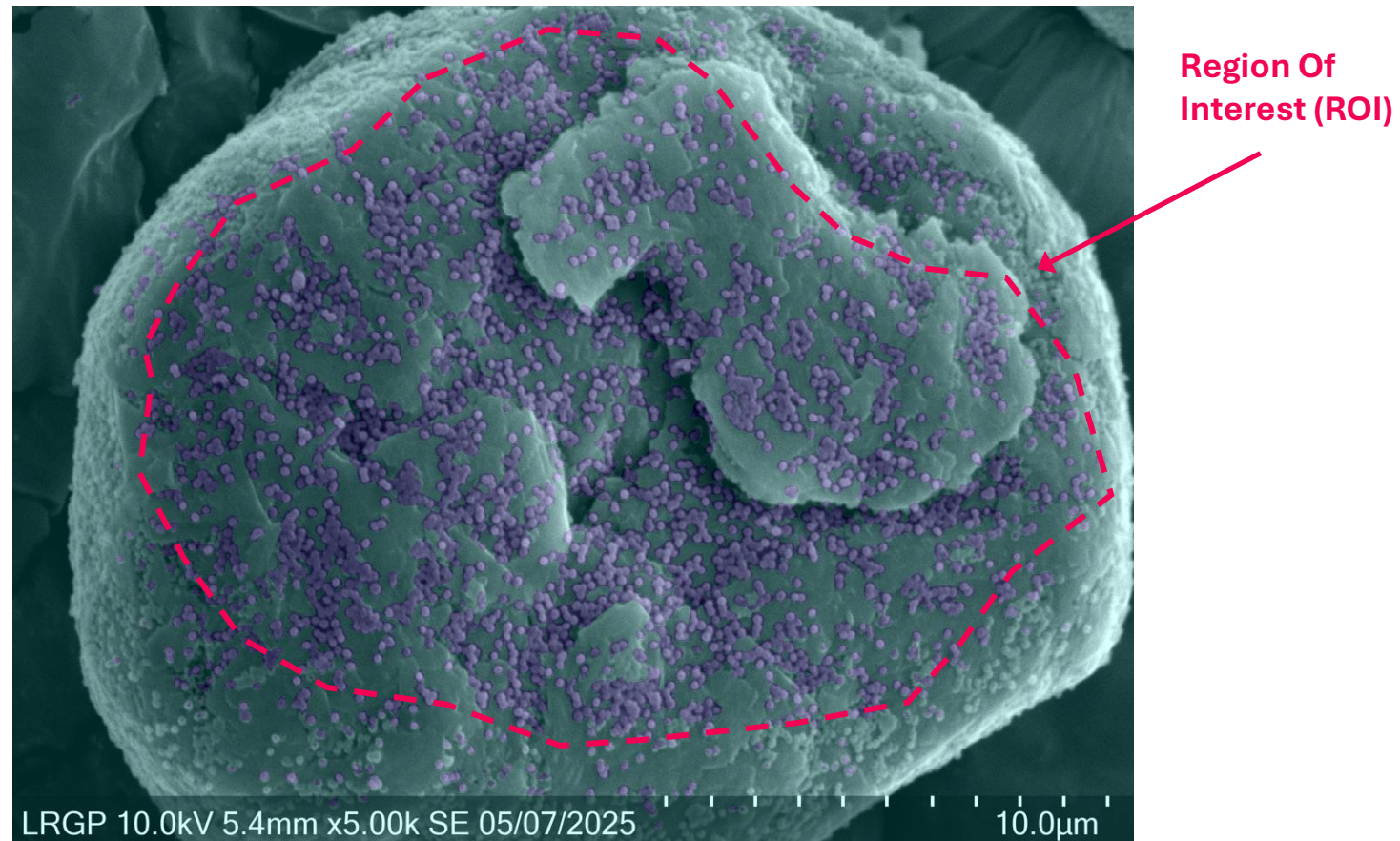
II – Mixing step study : key materials characteristics

III – Powder Surface Energy & Surface Coverage: aptitude to interact

IV – Conclusion and perspectives

II – Surface coverage : Definition and interest

- Surface coverage (SC) = $\frac{\sum_{ROI} A_{additives}}{A_{ROI}}$



Segmentation map and ROI of SEM micrograph of graphite particle covered by PVDF-1 (99:1 mixture)

II – Surface coverage calculation methods

Image analysis on SEM micrographs :

Threshold
method

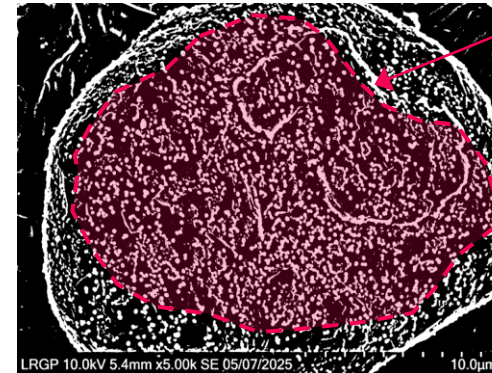
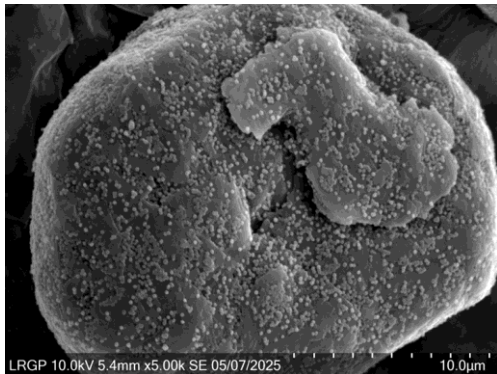


or

Neural network
training



Image processing +
Threshold

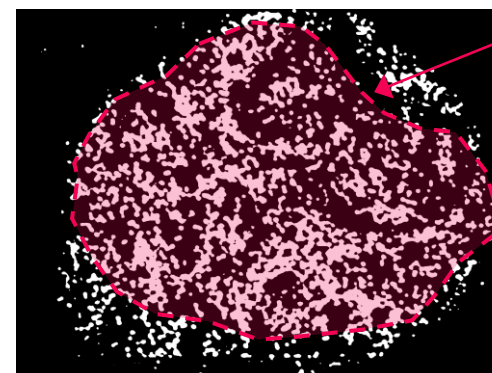
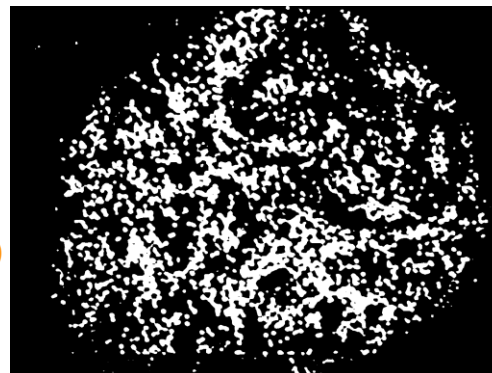


ROI

Surface coverage

Segmentation
(neural network)

x10 per mixture



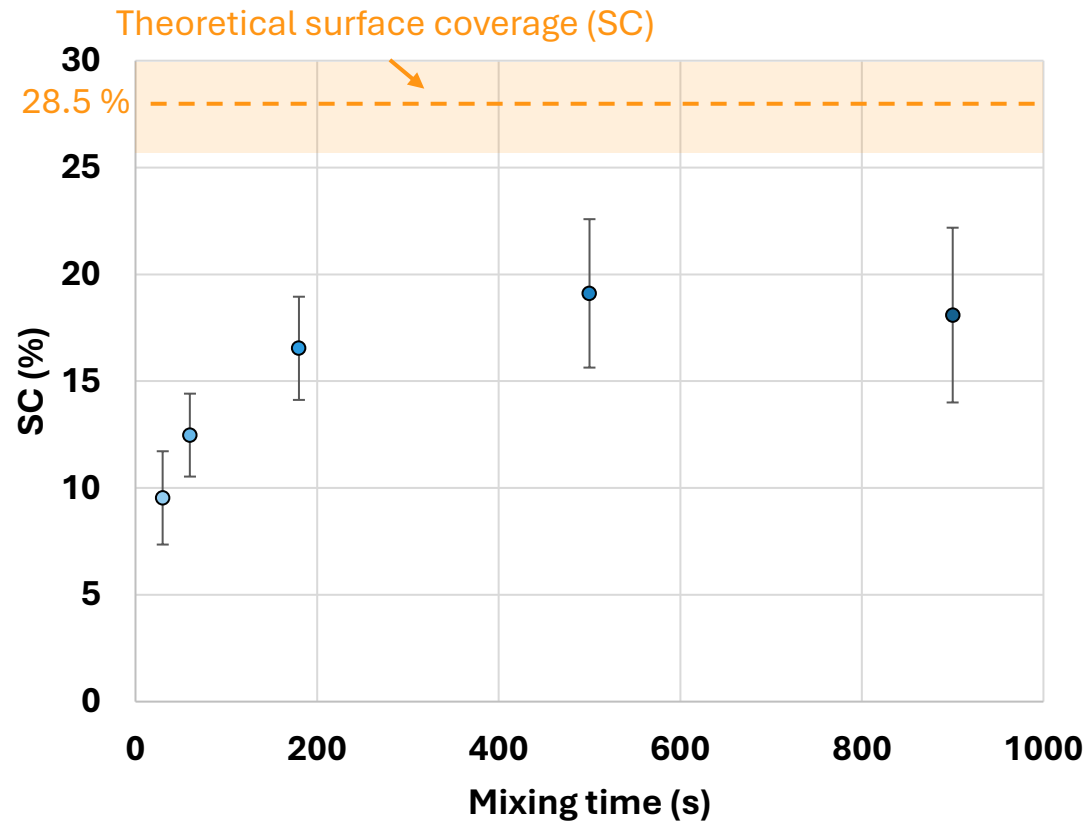
ROI

Surface coverage

II – Surface coverage over mixing time

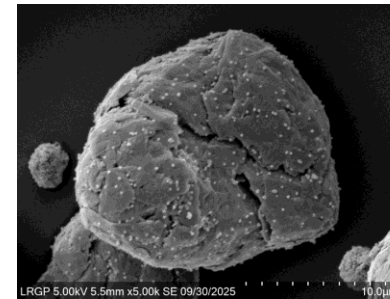
- Evolution of surface coverage over time for 99:1 Gr/PVDF-1 mixture :

Mixing time: 30, 60, 180, 500 and 900s

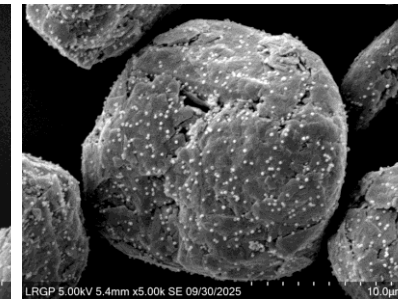


SEM micrographs of graphite particle covered by PVDF-1 for different mixing time :

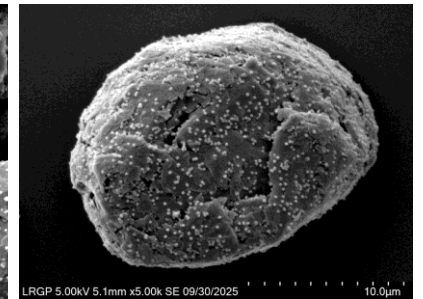
t = 30s



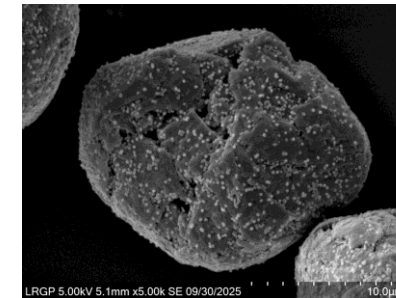
t = 60s



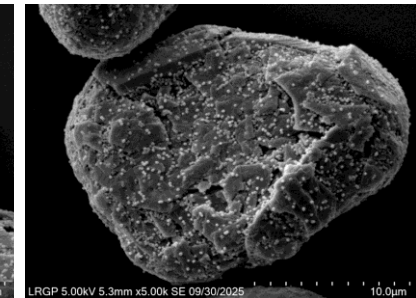
t = 180s



t = 500s



t = 900s



- In these mixing conditions, SC increases until reaching a limit after about 500 s
- Theoretical SC can be calculated from particles size and true density assuming all the PVDF particles covering Gr

Surface energy : Amount of energy needed to increase the solid surface by one unit

- Consequence of the anisotropic distribution of atomic bonds on material surface

$$\gamma_s = \gamma_s^{sp} + \gamma_s^d$$



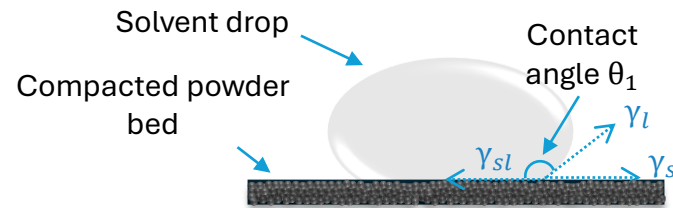
Specific Dispersive
(polar) (non-polar)

- Characterization of adhesive/cohesive behavior of the material

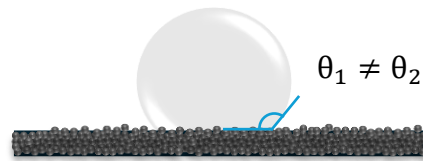
(Fowkes, 1964) $w_{ij} = 2 \cdot \left(\sqrt{\gamma_{s,i}^{sp} \cdot \gamma_{s,j}^{sp}} + \sqrt{\gamma_{s,i}^d \cdot \gamma_{s,j}^d} \right)$

II – Sessile drop : Dispersive surface energy

Principle of sessile drop technique for different powder bed compaction state :



Smooth surface



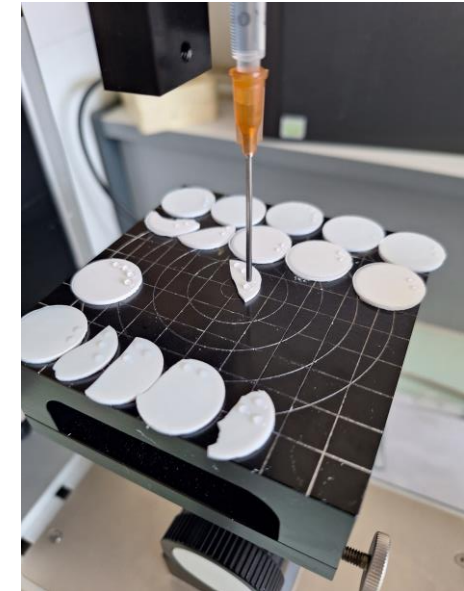
Rough surface

$$\text{(Young-Dupré)} \gamma_{sl} = \gamma_s - \gamma_l \cdot \cos(\theta) \quad (1)$$

$$\text{(OWRK method)} \gamma_{sl} = \gamma_s + \gamma_l - 2 \left(\sqrt{\gamma_s^{sp} \cdot \gamma_l^{sp}} + \sqrt{\gamma_s^d \cdot \gamma_l^d} \right) \quad (2)$$

$$\left. \begin{array}{l} (1) \\ (2) \end{array} \right\} \frac{\gamma_l \cdot (1 + \cos(\theta))}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^{sp}} \cdot \sqrt{\frac{\gamma_l^{sp}}{\gamma_l^d}} + \sqrt{\gamma_s^d}$$

Experimental setup :

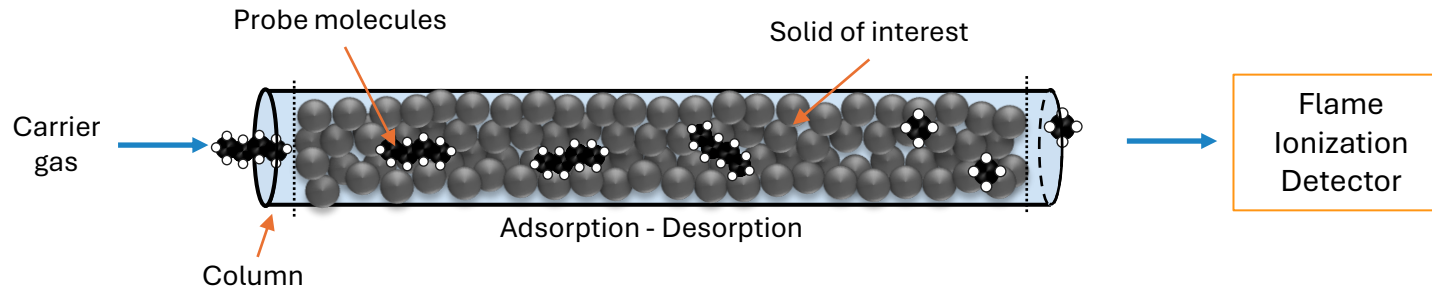


Material	PVDF-1	Graphite
γ_s^d (mJ/m ²) (sessile drop)	31.8	50.8 *

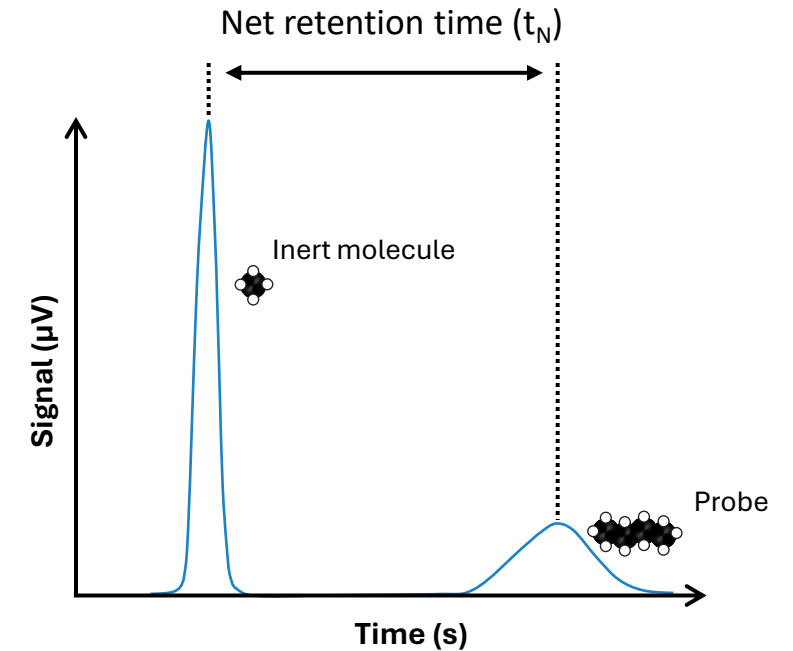
* Lee et al., 2017

II – Principle of Inverse Gas Chromatography (IGC) analysis

Principle of inverse gas chromatography (IGC) :



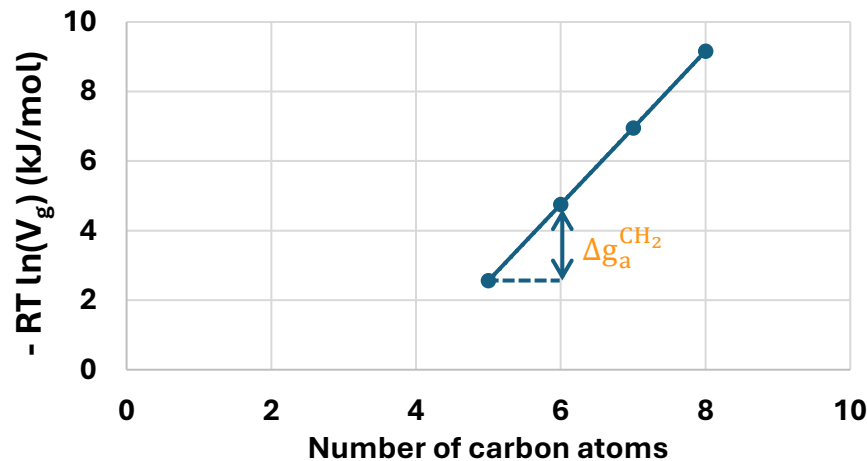
Chromatogram of a probe :



- Complete surface analysis :
 - **Dispersive surface surface energy (n-alkanes)**
 - Specific interaction parameter (polar probes)
 - Electron donor/acceptor behavior (Lewis acids and bases)
 - Nano-rugosity (branched/cyclic alkanes)

II – IGC-ID : Dispersive surface energy

Evolution of the free energy of adsorption of HSV900 as a function of the number of carbon atoms of n-alkanes (Dorris & Gray, 1979) :



$$\gamma_s^d = \frac{(\Delta g_a^{\text{CH}_2})^2}{4 \cdot (N_a \cdot a_{\text{CH}_2})^2 \cdot \gamma_{\text{CH}_2}^d}$$

With a_{CH_2} : methylene group surface area (m²)

$\gamma_{\text{CH}_2}^d$: methylene group dispersive surface energy (J/m²)



Material	PVDF-1	Graphite
γ_s^d (mJ/m ²) (IGC)	26.3	132.1
γ_s^d (mJ/m ²) (sessile drop)	31.8	50.8 *

* Lee et al., 2017

- Sessile drop : Compacted powder bed surface

- IGC-ID : Particle surface

I – Materials and methods

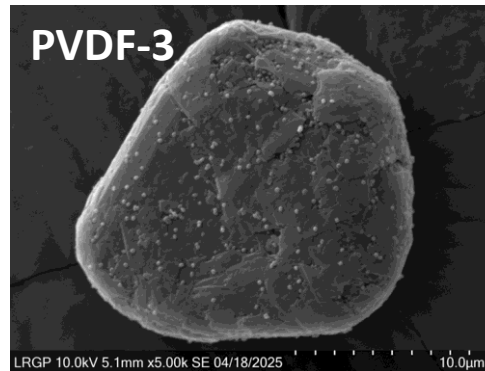
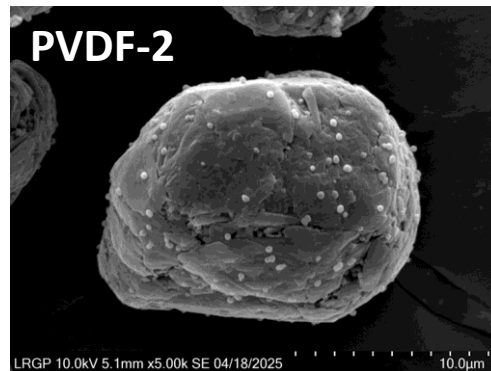
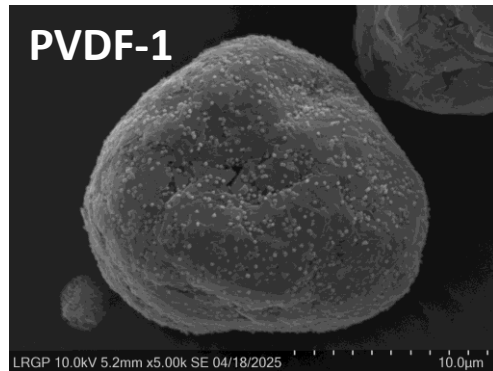
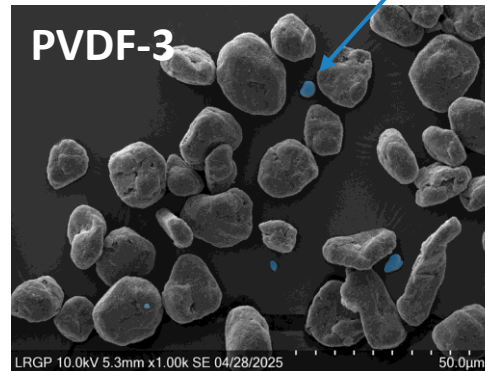
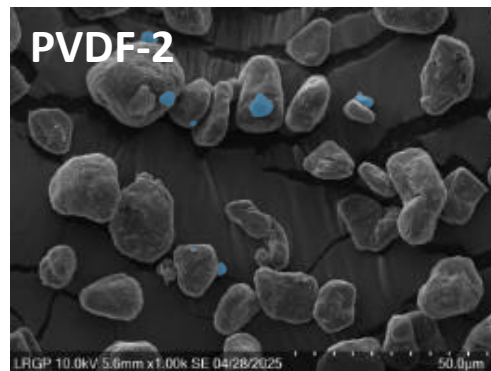
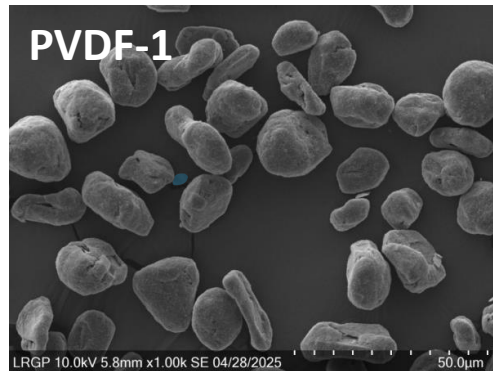
II – Mixing step study : key materials characteristics

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IV – Conclusion and perspectives

III – Surface coverage of 99:1 Gr/PVDF mixtures

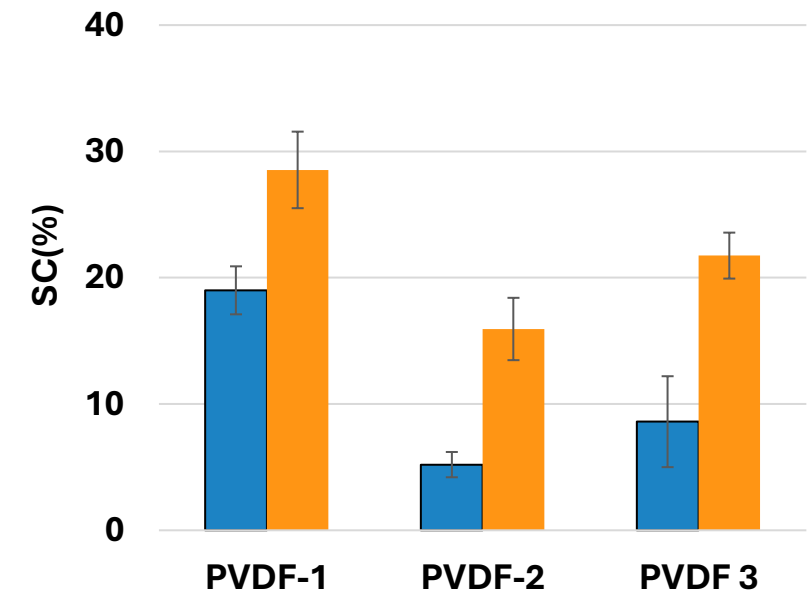
Mixing conditions: Gr/PVDF 99:1; impeller speed 3000 rpm; time 15 mn; T 25°C



Binder nature :

- PVDF-1
- PVDF-2
- PVDF-3

■ Experimental ■ Theoretical

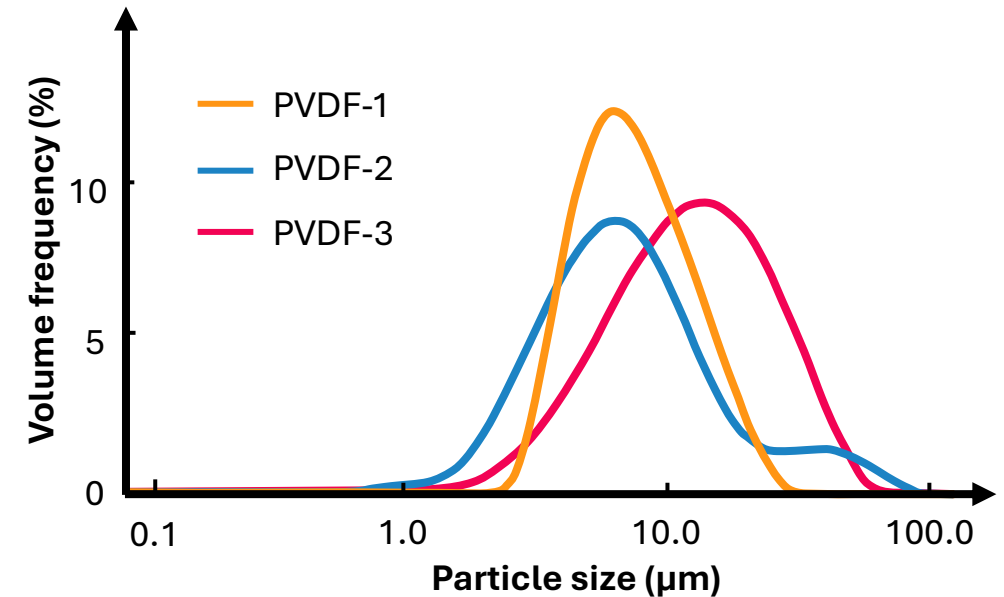


→ Surface coverage varies across the three mixtures, which indicates different particle arrangements

III – Influence of PVDF surface energy on surface coverage

- Particle size distribution of PVDF aggregates (laser granulometry; dispersion in water + 1% tween 80) :

	Gr	PVDF-1	PVDF-2	PVDF-3
SC (%)	x	19.0	5.2	8.6
γ_s^d (mJ/m ²)	132.1	26.3	21.3	27.9
Echange surface (m ² /g)	5.2	47.5	35.4	39.2
D ₅₀ (nm)	x	160	270	200



→ PVDF-2 has lower surface energy than PVDF-1 and -3

→ Binder surface energy and particle size have an influence on surface coverage

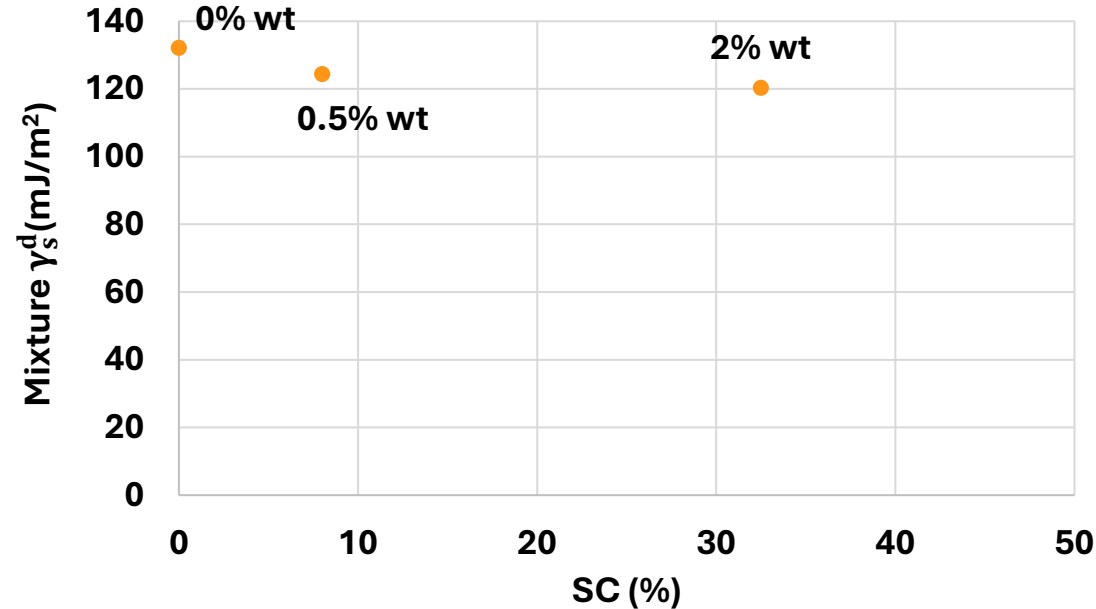
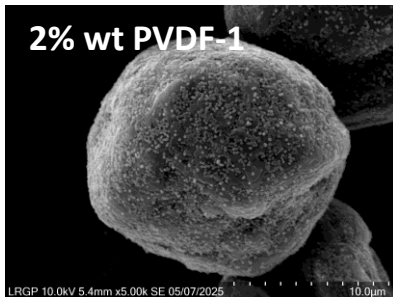
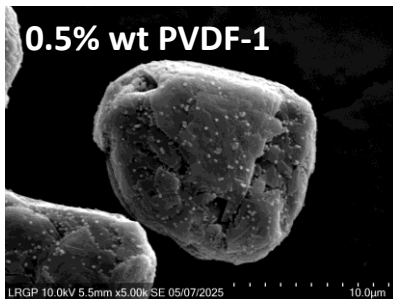
III – Effect of surface coverage on mixture surface energy (experimental)

- Measurement of mixture dispersive surface energy (γ_s^d) :

Mixing conditions: impeller speed 3000 rpm; time 15 mn; T 25°C

PVDF-1 %wt :

- 0.5 %wt
- 1% wt
- 2% wt



● Mixture γ_s^d

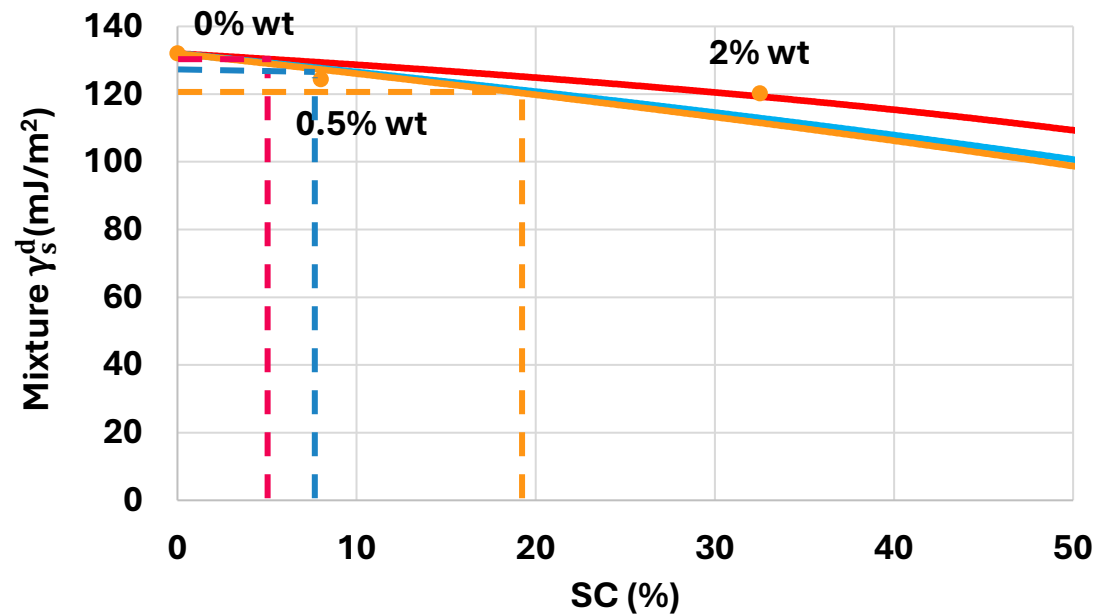
→ Increasing PVDF-1 %wt reduces mixture γ_s^d

III – Effect of surface coverage on mixture surface energy (model)

- Calculation of Gr/PVDF-1 99:1 mixture γ_s^d :

Hypothesis : All of the binder is deposited on graphite surface

$$V_g(\text{mixture}) = SC \cdot V_g(\text{PVDF}) + (1 - SC) \cdot V_g(\text{Gr})$$



- Gr/PVDF-1 mixture γ_s^d (IGC)
- Predicted Gr/PVDF-1 γ_s^d
- Predicted Gr/PVDF-2 γ_s^d
- Predicted Gr/PVDF-3 γ_s^d

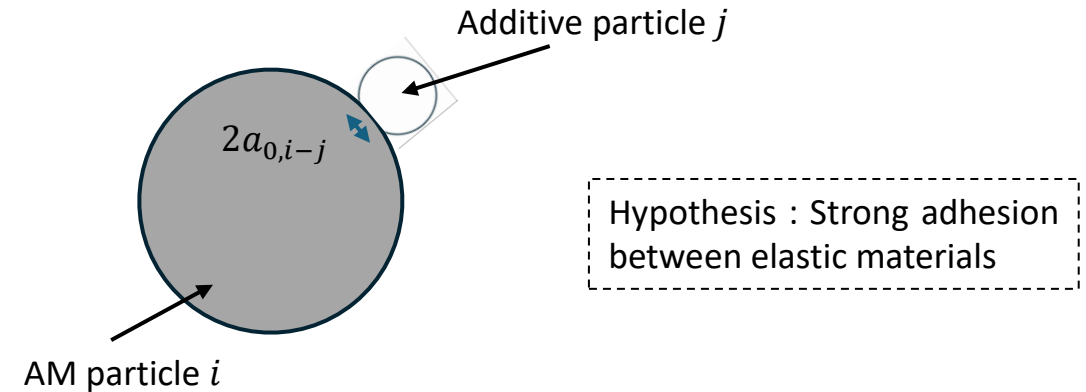
- For low binder content, mixture γ_s^d can be modeled from graphite and PVDF net retention volume
- Gr/PVDF 99:1 mixture γ_s^d can be estimated using the model

III – Interaction energy calculation : JKR model

- Johnson, Kendall & Roberts, 1971 : $a_{0,i-j} = \left(\frac{9\pi w_{ij} R^2}{2E^*} \right)^{1/3}$

with $w_{ij} = 2 \cdot \sqrt{\gamma_i^d \cdot \gamma_j^d}$

- Adhesion/cohesion energy: $E_{i-j} = w_{ij} \cdot (\pi \cdot a_{0,i-j}^2)$



- Ludwig et al., 2017 : Prediction of additives particle arrangement after dry mixing

$$\Delta E = E_{i-j} - 6 \times E_{j-j}$$

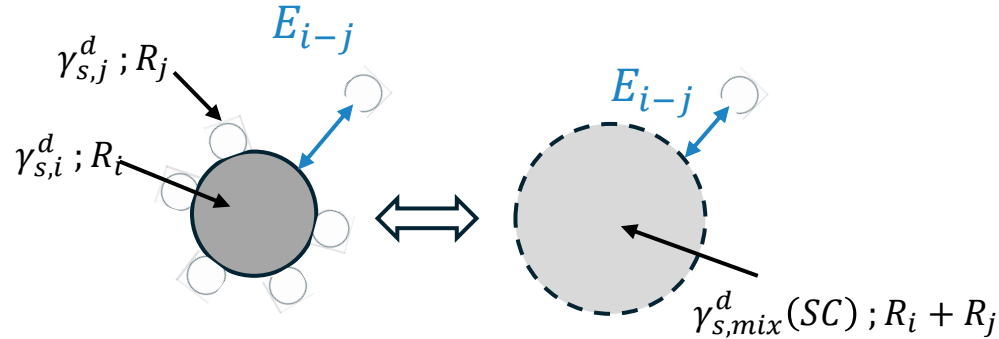
$$\Delta E < 0 \rightarrow \text{Coating}$$

$$\Delta E > 0 \rightarrow \text{Aggregation}$$

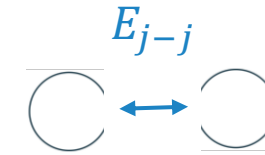
$$\left. \begin{array}{l} \Delta E < 0 \rightarrow \text{Coating} \\ \Delta E > 0 \rightarrow \text{Aggregation} \end{array} \right\} \text{Equilibrium : } E_{i-j} = 6 \times E_{j-j}$$

III – Comparison of interaction energy

Adhesive interaction (Gr+PVDF/PVDF)



Cohesive interaction (PVDF/PVDF)



Mixing conditions: Gr/PVDF 99:1; impeller speed 3000 rpm; time 15 mn; T 25°C

Hypothesis : equilibrium between coating and aggregated PVDF

Binder	PVDF-1	PVDF-2	PVDF-3
Mixture γ_s^d (mJ/m ²) (predicted)	120.4	130.1	127.3
$E_{(Gr+PVDF)/PVDF}$ (J)	6.14E-17	1.13E-16	9.40E-17
$E_{PVDF/PVDF}$ (J)	1.02E-17	1.50E-17	1.58E-17
$\frac{E_{(Gr+PVDF)/PVDF}}{E_{PVDF/PVDF}}$ (J)	6.01	7.56	5.97

→ Comparison between (Gr+PVDF)/PVDF and PVDF/PVDF interaction energy using JKR model and mixture suggests that equilibrium between coating and aggregated PVDF is reached for PVDF-1 and -3

I – Materials and methods

II – Mixing step study : key materials characteristics

III – Powder surface energy & surface coverage: aptitude to interact

IV – Conclusion and perspectives

- ❑ Surface coverage quantifies additive particle arrangement during mixing step
- ❑ Surface energy partly governs interaction energy between particles, which is the source of particle rearrangement during mixing
- ❑ During mixing, graphite is coated until its surface energy reaches a certain limit, depending on the nature of the materials. At this point equilibrium between aggregated and covering PVDF content is reached based on adhesive and cohesive interaction

Thank you

Alex Lemarinel^{1,2}, Maria Graciela Cares¹, Jesus Alberto Barreras Uruchurtu², Clément Paul³, Thomas Philippe², Véronique Falk¹

(1) Laboratoire Réactions et Génie des Procédés,
Université de Lorraine - CNRS, Nancy, France



(2) Ampère (Renault Group), Lardy, France



AMPERE

(3) Arkema, Serquigny, France

ARKEMA

Slide 12 :

F. M. Fowkes, « Attractive forces at interfaces », *Ind. Eng. Chem.*, vol. 56, n° 12, p. 40-52, déc. 1964, doi: [10.1021/ie50660a008](https://doi.org/10.1021/ie50660a008).

Slide 13:

J. Lee et B. Lee, « A simple method to determine the surface energy of graphite », *Carbon letters*, vol. 21, p. 107-110, janv. 2017, doi: [10.5714/CL.2017.21.107](https://doi.org/10.5714/CL.2017.21.107).

Slide 21:

K. L. Johnson, K. Kendall, et A. D. Roberts, « Surface energy and the contact of elastic solids », *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, vol. 324, n° 1558, p. 301-313, sept. 1971, doi: [10.1098/rspa.1971.0141](https://doi.org/10.1098/rspa.1971.0141).

B. Ludwig *et al.*, « Understanding Interfacial-Energy-Driven Dry Powder Mixing for Solvent-Free Additive Manufacturing of Li-Ion Battery Electrodes », *Advanced Materials Interfaces*, vol. 4, n° 21, p. 1700570, 2017, doi: [10.1002/admi.201700570](https://doi.org/10.1002/admi.201700570).