Comparison of spray retention on synthetic superhydrophobic surface with retention on outdoor grown wheat leaves

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Context

• High pressure from all stakeholders to decrease application rates of the few approved active substances

• The challenge is therefore to further improve the efficiency of the application process

• Application process is usually divided in 4 stages: deposition, retention, uptake and translocation.

• One mean is to improve retention that is defined as the quantity retained on the plant.
Context

• Retention results from the combination of numerous physical parameters involved:
  – Drops speed and diameter
  – Mixture physico-chemical properties as surface tension and viscosity
  – Leaf angle
  – Canopy density
  – Leaf wettability
• Plants exhibit various degrees of wettability from very-easy to very-difficult-to-wet depending on plant species, grow stage, age...
Context

- Very difficult-to-wet species with thin leaves as wheat or black-grass are amongst the most challenging targets for efficient pesticide application because of superhydrophobicity.
Superhydrophobicity

Natural

Artificial
Context

• Superhydrophobicity appears on hydrophobic materials when the apparent contact angle is enhanced by the small scale roughness of surface that dramatically increase their specific surface. For leaves if originates from cuticle pattern, waxes, hairs,..
Context

- Two models are classically used by physicists to describe the wetting of artificial superhydrophobic surfaces
  - The Wenzel non-composite regime also referred as pinning, characterized by the sticking of the liquid which is anchored in the surface cavities
  - The Cassie-Baxter composite regime, where the liquid stands on the pillars of the surface and some air is trapped beneath in the valleys of the structure
Context

- On the basis of these wetting regime, different outcomes during impact have been identified by physicists as a function of drop size and velocity (Weber number) and surface roughness.
Objectives

• As impact outcome is a function of droplet speed and diameter, surface hydrophobicity and spray liquid physicochemical properties, the study of retention improvement using additives must:
  – be conducted using realistic droplet diameter and speed,
  – be performed on a well characterized reference surface, representative of difficult-to-wet leaves
  – Identify the different outcomes as a function of speed and diameter.
Objectives

• There is a need for a reference surface to classify effect of pesticide formulations and additives on retention for difficult-to-wet surfaces

• Outdoor grown wheat leaves (*Triticum aestivum* L. cv Julius) will be compared to a commercial Teflon based synthetic super hydrophobic surface (thermo Scientific X2XES2013BMNZ)
Material and methods

- Usually impact studies are conducted using on demand monodisperse drop generators but it is limited to settling speed.
Material and methods

- A method was developed to record impact of droplets originating from a moving agricultural nozzle with a 1 mm slit and a 10*2 mm² field of view.
Material and methods

• Videos are recorded at 20000 fps, teflon slide, XR11003 0,3MPa
Material and methods

• About 10 to 50 impact are recorded in the field of view, depending on the drop spectra
• Image analysis software to get a measurement of drop speed and size before impact.
• The operator identifies the impact outcome according to the physical classification
Material and methods

• A log-log scale graphic is built with a color code
  – adhesion
  – rebound (● for cassie-Baxter, ○ for Wenzel)
  – fragmentation ( + for Cassie-Baxter, * for Wenzel)

• Logistic regression is used to identify the boundaries between impact outcomes as a function of the Weber number
Results

• XR 11003 Nozzle, 0.3 MPa, 2m/s on *Triticum aestivum* L. cv Julius) and (thermo Scientific X2XES2013BMNZ

• A trisiloxane tank-mix adjuvant (Break-Thru S240, Evonik Industries AG) was sprayed on target surfaces at 3 concentrations in distilled water: 0.025, 0.05 and 0.1% V/V. Distilled water was tested as a reference

<table>
<thead>
<tr>
<th></th>
<th>Distilled water</th>
<th>BT 0,025%</th>
<th>BT 0,05%</th>
<th>BT 0,1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static surface tension</td>
<td>0,072</td>
<td>0,023</td>
<td>0,022</td>
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</tbody>
</table>
Results for distilled water

Synthetic super hydrophobic Teflon slide

- Adhesion
- Rebound
- Splashing
- Secondary impacts

We=0.2
We=70
Results for distilled water

- On the teflon slide, the different outcomes are sharply separated by Weber boundaries. Outcome distributions are characteristic of the theoretical high Wenzel roughness behaviour. Only a few drops were deposited in the Cassie-Baxter regime and most drops bounced. Some drops came back in the field of view and undergo a secondary impact. The most energetic drops splash at impact.
Results for distilled water

*Triticum aestivum* L. cv Julius
Results for distilled water

• At first glance, the behaviour on the wheat leaves presents a much wider variability. However, clear similarities appear when examined more closely.
  – Rebound still occurs for a wide range of Weber numbers but deposits appear probably because of the natural surface heterogeneity. This may also be related to dirt as it well established that superhydrophobicity is very sensitive to any soiling of the surface.
  – The splashing boundary is quite similar, what is consistent is the fact that this boundary is known to be less related to the surface properties than to the fluid rheology.
Results for BT 0.025%

Synthetic super hydrophobic Teflon slide

*Triticum aestivum* L. cv Julius
Results for BT 0.05%

Synthetic super hydrophobic Teflon slide

Triticum aestivum L. cv Julius
Results for BT 0.1%

Synthetic super hydrophobic Teflon slide

Triticum aestivum L. cv Julius

On both surfaces, splashing is replaced by a pinning fragmentation at the higher surfactant concentration.
Results for surfactant formulations

• On the Teflon slide, increasing the surfactant concentration leads progressively to the vanishing of the rebound events. Complete extinction is observed for the highest concentration tested, 0.1% surfactant solution.

• It is observed that at 0.025% the remaining rebound events are surrounded by adhesions. The high Weber number adhesion probably corresponds to the pinning caused by a Cassie-Baxter to Wenzel transition resulting from the impact energy and surfactant effect.

• Splashing occurred at a slightly lower Weber number with increasing surfactant concentration.

• On the wheat leaf, a higher variability of the outcome of impacts was observed but rebound disappeared for lower Weber numbers. The observed variability was not found related on the location of the impact on the leaf but seems related to variability between leaves. It is suspected that it originates from fouling differences between outdoor grown leaves.
## Results for surfactant formulations

Volumetric presentation of the impact outcome (tedious because of the relatively low number of droplets)

<table>
<thead>
<tr>
<th></th>
<th>Distilled water</th>
<th>BT 0,025%</th>
<th>BT 0,05%</th>
<th>BT 0,1%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Teflon slide</strong></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>%vol adhesion</td>
<td>4,26</td>
<td>28,83</td>
<td>38,68</td>
<td>52,63</td>
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<tr>
<td>%vol rebound</td>
<td>70,12</td>
<td>12,27</td>
<td>2,58</td>
<td>/</td>
</tr>
<tr>
<td>%vol fragmentation</td>
<td>25,62</td>
<td>58,9</td>
<td>58,74</td>
<td>47,37</td>
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<td><strong>Wheat leaf</strong></td>
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<td></td>
<td></td>
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<tr>
<td>%vol adhesion</td>
<td>25,06</td>
<td>19,45</td>
<td>26,85</td>
<td>38,6</td>
</tr>
<tr>
<td>%vol rebound</td>
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<td>13,77</td>
<td>12,6</td>
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<tr>
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<td>47,62</td>
<td>60,64</td>
<td>59,38</td>
<td>48,8</td>
</tr>
</tbody>
</table>
Discussion

• Results highlight similarities between drop behaviour during impact on the synthetic superhydrophobic surface and wheat leaves.

• The possible outcomes of impact are consistent with theoretical developments on superhydrophobic materials.

• Future work will focus on different surfactants presenting various dynamic surface tensions (DST) as the time scale of drop deformation during impact is very low (< 5 ms).

• Other rheological properties will also be investigated as the use of non-Newtonian fluids is a promising way to reduce fragmentation.

• Leaves present an anisotropic surface that influences the impact outcome, satellite drops being directed preferentially along the main axis.

• Leaf angle effects will be studied further.

• Fouling is suspected to reduce drastically rebound in some practical application on outdoor grown leaves.