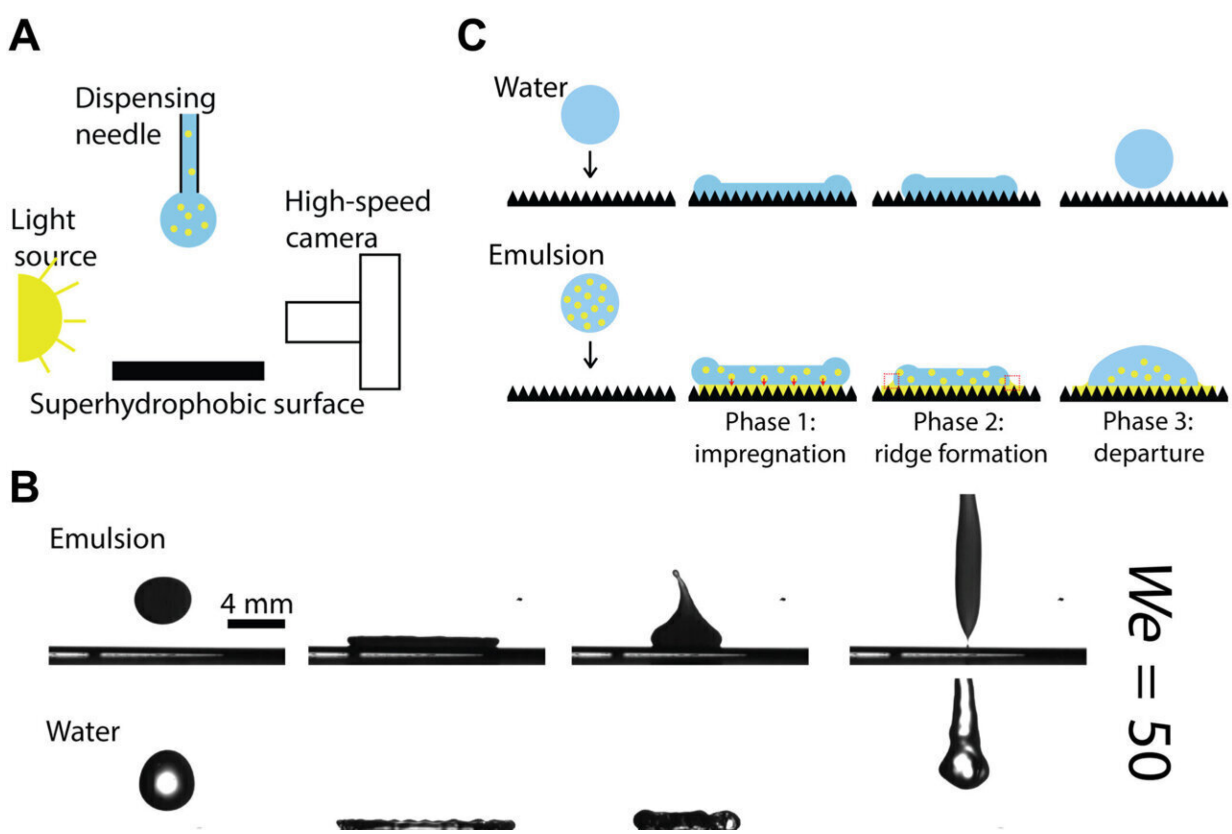
Dynamics of an impacting emulsion droplet: The influence of materials science in agriculture

March 28 2022, by Thamarasee Jeewandara



Impacts of water droplets and oil-in-water emulsion droplets on superhydrophobic surfaces. (A) Schematic of experimental setup. (B) Snapshots of high-speed videos of emulsion and water droplets impacting on a surface. The emulsion is a hexadecane-in-water emulsion at a concentration of 20%. At We = 50, both droplets bounce. At We = 87, water bounces while the emulsion sticks. At We = 95, both droplets splash and bounce. (C) Schematic of water and emulsion impact dynamics showing the three phases: impregnation, oil ridge formation, and departure. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abl7160

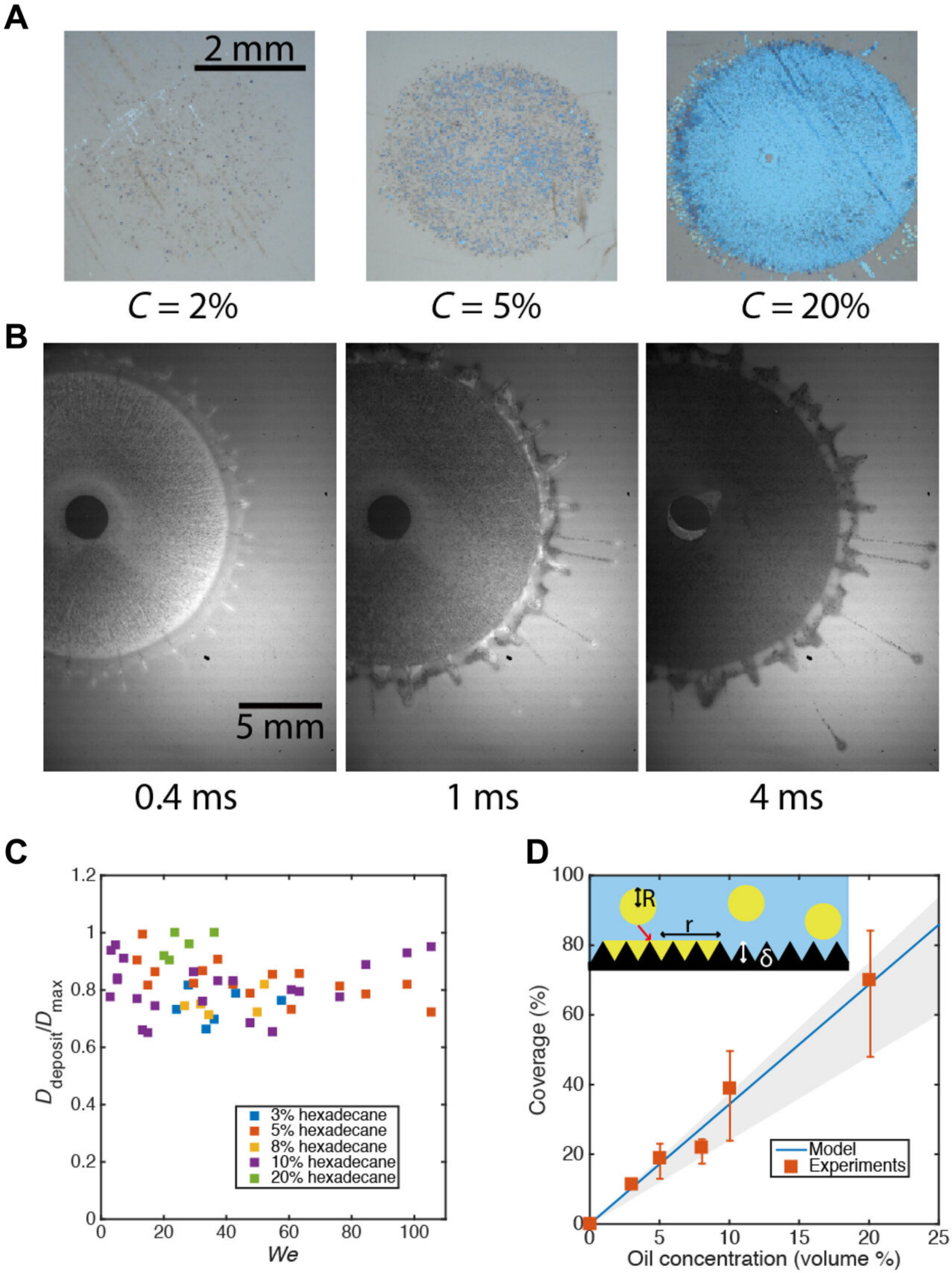
Emulsions of oil-based pesticides are widely used in agriculture, although they are a major environmental and health hazard because they bounce off plant surfaces due to their hydrophobic nature, resulting in the pollution of water and soil. In a new report, Maher Damak and a team of scientists in mechanical engineering at MIT described an unexpected transition from bouncing to sticking to bouncing, with accelerated impact speed of the droplet. The team highlighted the underlying physics of the phenomenon and demonstrated the process by regulating a careful balance of three time scales: the time of droplet contact, time of oil impregnation and the formation of the oil ridge. They then built a design map to accurately regulate droplet bouncing and oil coverage. The research is now published in *Science Advances*.

Using materials science for environmentally optimized agriculture practices

Emulsion sprays are crucial in industries and agriculture sprays commonly include oil-in-water emulsions containing emulsifiable concentrates with an active pesticide ingredient in the oil phase mixed with water. In this instance, the oil droplets are usually in the micron-scale range, therefore emulsions can be atomized and sprayed onto plants. However, the lack of retention of agricultural sprays on hydrophobic plants is a major limitation that can cause large-scale pollution. Materials scientists have extensively studied the droplet impacts of pure liquids on superhydrophobic surfaces. Researchers have used surfactants to reduce surface tension and thereby reduce droplet bouncing, however, they are less effective. In this work, the research team studied the impact of emulsion droplets on superhydrophobic surfaces.

Lead author and postdoctoral fellow Maher Damak, who is affiliated to the MIT Varanasi Group of Professor Kripa Varanasi, and is also the CEO and co-founder of Infinite Cooling, described the motivation behind their study, saying, "The research was motivated by the fact that there is a lot of pesticide waste due to droplets bouncing off plant surfaces as they are sprayed. ... the method we developed in this study uses oil emulsions to mitigate the issue, by allowing droplets to stick on hydrophobic plant surfaces."

The team showed how metastable emulsions containing a pesticide carrier oil and water alone can be effective when used with the right emulsion and spraying parameters. The introduction of surfactant-free sprays in agriculture can prevent the spread of large-scale toxic chemicals in the environment and reduce costs in agriculture.


A
2 mm
C = 2%
C = 5%
C = 20%
B
5 mm
0.4 ms
1 ms
4 ms
C
D_deposit/D_max
We
3% hexadecane
5% hexadecane
8% hexadecane
10% hexadecane
20% hexadecane
D
R
r
δ
Coverage (%)
Oil concentration (volume %)
Model
Experiments

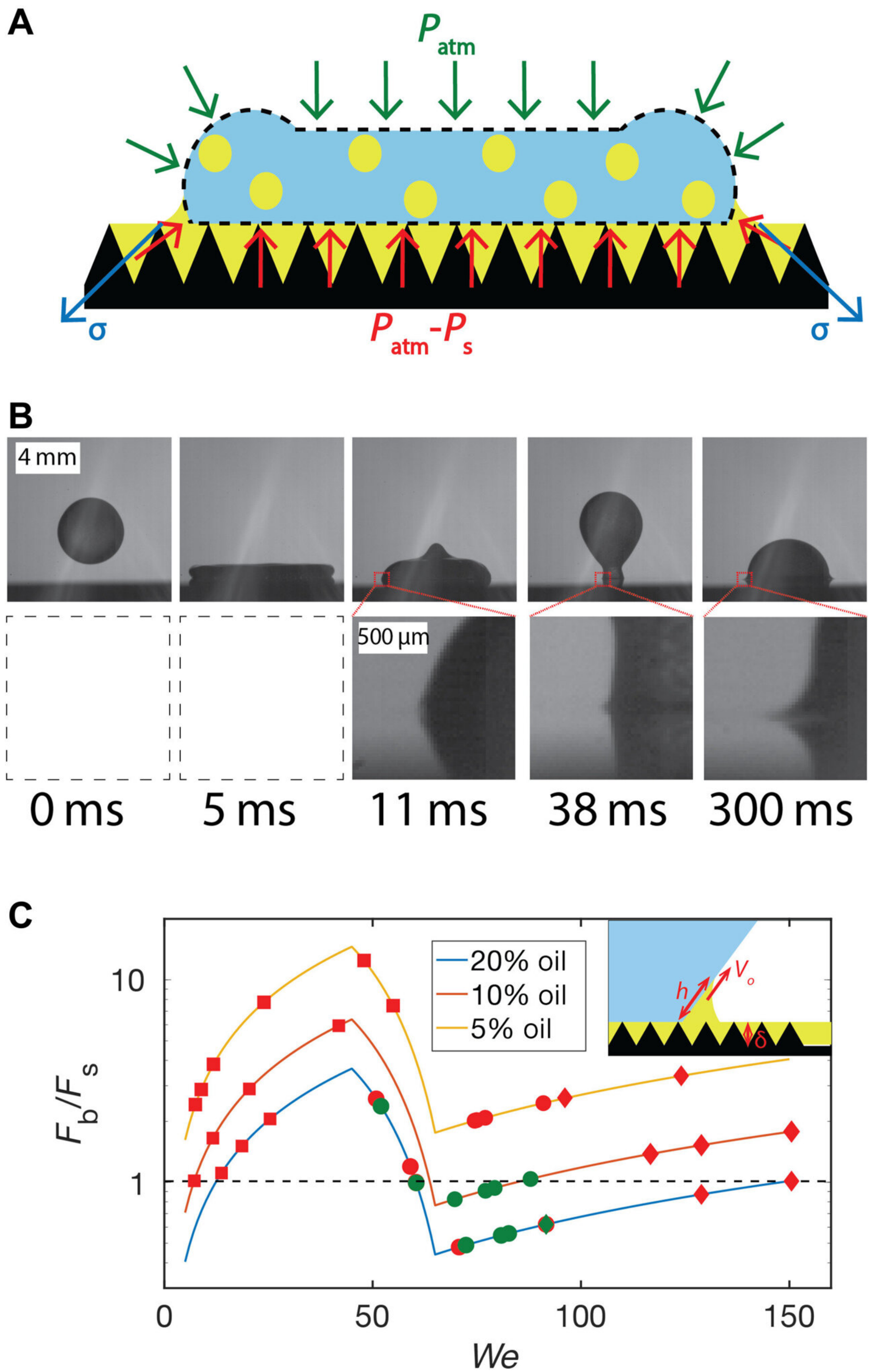
Oil impregnation of surfaces during emulsion impacts. (A) Microscope images of surface after impacts of emulsion droplets with various concentrations on inclined superhydrophobic surfaces at We = 30. (B) Snapshots of high-speed bottom-view videos of the spreading phase of a 20% hexadecane-in-water emulsion droplet impact on a transparent superhydrophobic surface (We = 60). The focus of the lens is on the interfacial plane between the droplet and the surface. The black dots are oil droplets depositing on the surface. (C) Experimental measurements of normalized deposit diameter as a function of the Weber number for various concentrations of oil-in-water emulsions. (D) Oil coverage of the surface after impact. Symbols are experimental measurements (SD from six repeated experiments with varying We between 10 and 40), and the solid line is our model prediction. The shaded gray area shows model predictions for oil droplet radii ranging from 400 to 900 nm. The inset is a schematic of the change in shape of oil droplets when they impregnate the surface. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abl7160

Emulsion droplet impacts

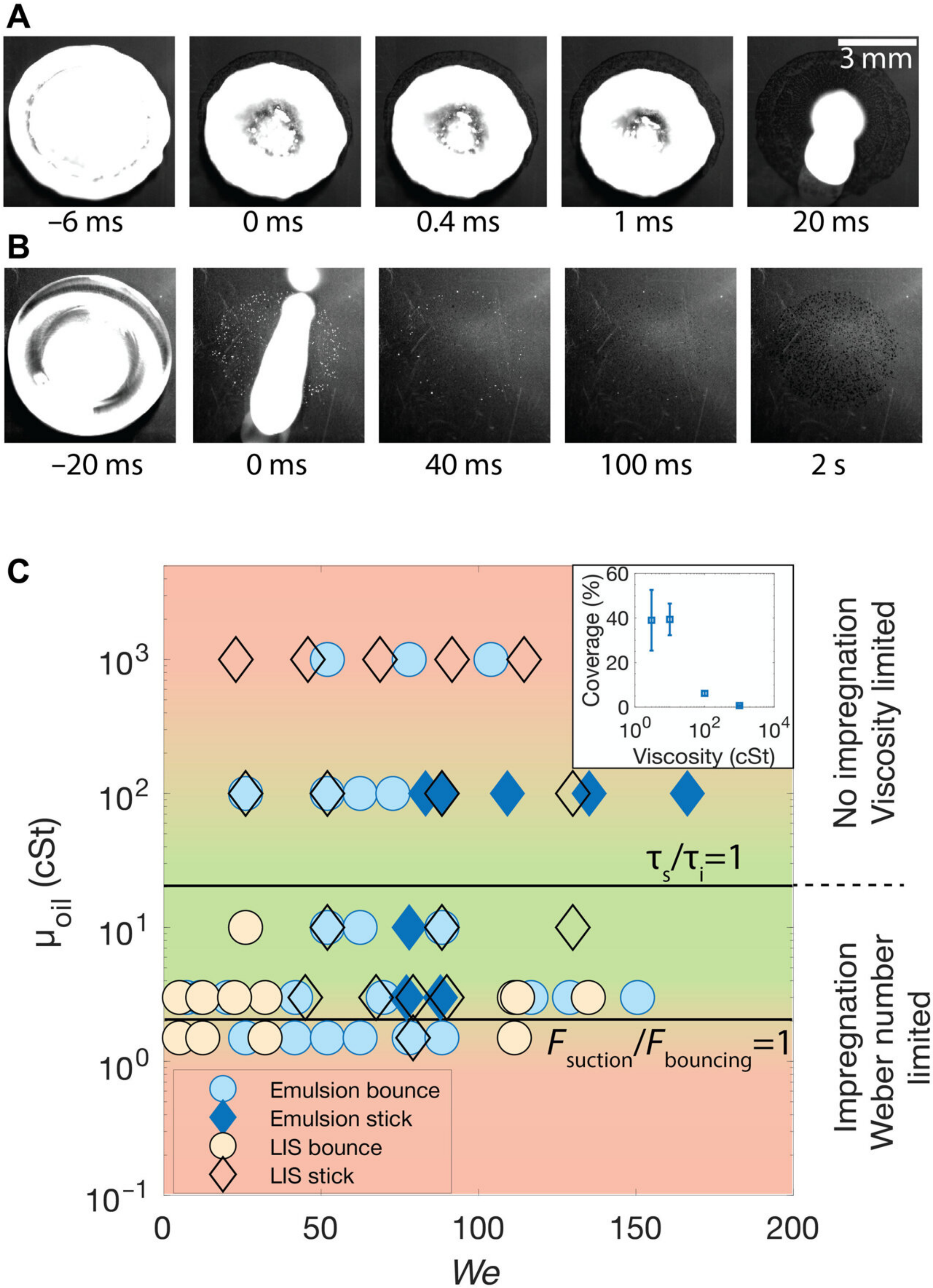
The scientists studied the behavior of emulsion droplet impacts by mixing the model oil hexadecane with water, and used a probe sonicator to produce an oil-in-water emulsion for agricultural sprays. They used hexadecane as a model and did not include surfactants, to prove that surfactant-free formulations can effectively ensure droplet retention. The surfactant-free emulsions were metastable for more than three hours—longer than the typical duration of agricultural sprays. Damak highlighted the significance of this method: "Many pesticides are already sprayed as oil emulsions and this work can allow growers to tune the parameters of these emulsions to make them much more effective, without adding any other chemicals." Emulsions can therefore be made at the farm and sprayed while they are still stable. In the experimental setup, the team used a needle to dispense droplets on a superhydrophobic surface and varied the oil concentration in the emulsion with the goal to retain the carrier water droplets, while the pesticide molecules reached the plant surface. The team explained the phenomenon via a three-phase mechanism.

Experimental steps: Oil impregnation, ridge formation, bouncing-sticking-bouncing transition

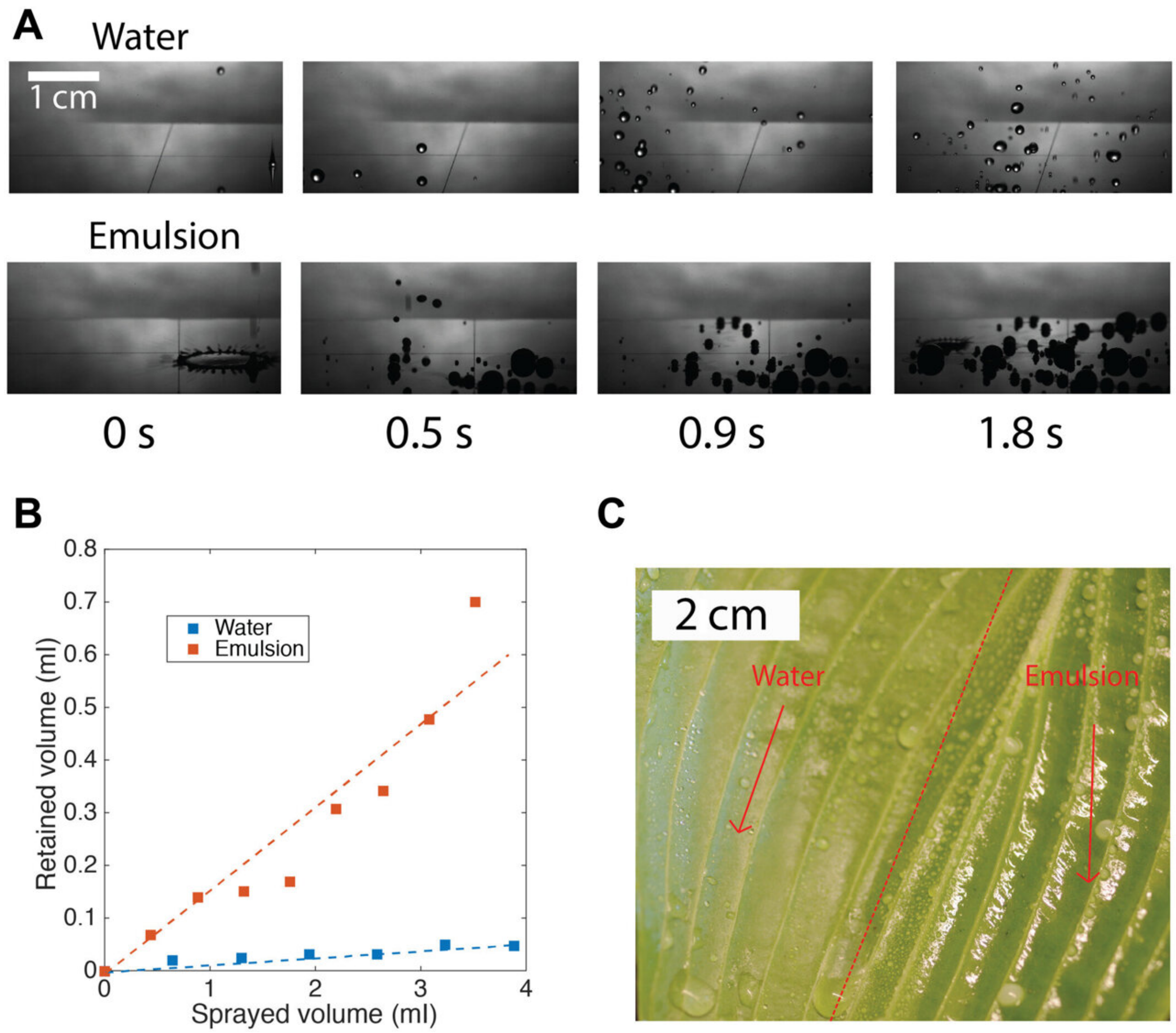
Damak et al. imaged the surface after the impact of an oil-in-water emulsion droplet, using an optical microscope. During the second phase, they noted the formation of an oil ridge around the emulsion droplet. As the emulsion droplet receded, the team noted a surface partially filled with oil. At the completion of this phase, they observed a suction force exerted by the droplet to prevent it from bouncing. As the surface energy converted back into kinetic energy, the emulsion droplet started accelerating vertically with a typical "bounce acceleration equivalent force." The researchers understood the origin of the bouncing-sticking-bouncing transition relative to Weber numbers; a parameter representing the ratio of disruptive hydrodynamic forces to the stabilizing surface tension force. "We found that the emulsified oil can deposit on the surface during the timescale of the impact and exert a suction force on the droplet, preventing it from bouncing off the surface," Damak said.


A
Patm
σ
Patm-Ps
σ
B
4 mm
500 µm
0 ms
5 ms
11 ms
38 ms
300 ms
C
20% oil
10% oil
5% oil
h
Vo
δ
Fb/Fs
10
1
0
50
100
150
We

Bouncing-sticking-bouncing transitions. (A) Schematic of a free-body diagram of a droplet retracting after impact, showing the pressure exerted by the atmosphere, the pressure exerted by the oil layer underneath, and the surface tension force along the contact line. (B) Snapshots of a water droplet with 10% hexadecane impacting with a Weber number of 24. The first row has photographs of the entire droplet in various stages, and the second row has zoomed-in photographs showing the oil ridge whenever visible. (C) Values of the calculated force ratio of the bouncing force to the sticking force in emulsion impacts experiments with various concentrations (left y axis) as a function of the experimental Weber number. Green symbols represent sticking droplets, while red symbols represent bouncing droplets. Line colors represent different oil concentrations. Shapes represent different instability patterns (squares for no instability, diamonds for splashing, and circles for rim instability and onset of splashing). The solid lines are model estimates of force ratios for three oil concentrations based on the derived equation for the force ratio. The dashed black line indicates a force ratio of 1, which is the theoretical transition from bouncing to sticking. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abl7160


A
3 mm
−6 ms
0 ms
0.4 ms
1 ms
20 ms
B
−20 ms
0 ms
40 ms
100 ms
2 s
C
Coverage (%)
Viscosity (cSt)
μoil (cSt)
We
τs/τi=1
Fsuction/Fbouncing=1
No impregnation
Viscosity limited
Impregnation
Weber number limited
Emulsion bounce
Emulsion stick
LIS bounce
LIS stick

Impregnation of surfaces by impacting emulsion droplets and effect on bouncing/sticking transition. (A) Snapshots of top-view high-speed video of a 10-cSt silicone oil in water emulsion impacting on a surface at We = 27. (B) Snapshots of top-view high-speed video of a 1000-cSt silicone oil in water emulsion impacting on a surface at We = 24. (C) Experimental impact outcomes of oil-in-water emulsions of various viscosities on superhydrophobic surfaces and of water droplets on liquid-impregnated surfaces (LIS) with lubricating oils of various viscosities. The lower solid line shows the limit below which maximal suction forces do not overcome the droplet inertia and where bouncing is expected to always occur for emulsions. The higher solid line shows the viscosity limit above which oil droplets in the emulsion do not have time to impregnate the surface during the contact time and the surface during the retraction phase diverges from an LIS-like surface. Inset: Surface coverage directly after rebound for different viscosity oils at a concentration of 10%. Other data points are silicone oils at various viscosities. The data were collected for We = 30 and We = 50, and there was no dependence of the Weber number. Error bars indicate the SD over 10 measurements for silicone oil and 6 measurements for hexadecane. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abl7160



Macroscopic spraying of emulsion on nonwetting surfaces. (A) Snapshots of high-speed video of water and emulsion (8% hexadecane in water) sprays on superhydrophobic surfaces. Spray droplets are on the order of 1 mm in diameter. Weber numbers were mostly in the 40-to-200 range. All water droplets bounce, while emulsion drops stick and accumulate on the surface (see movies S9 and S10). (B) Graphs of retained volume of sprayed liquid on superhydrophobic surface after repeatedly spraying fixed amounts of water and 20% hexadecane emulsions. Dashed lines are linear fits. The slope of the red dashed line corresponding to the emulsion case is 10 times larger than the slope of the water line. (C) Photograph of a hosta leaf after spraying the left side with water and the right side with a 20% hexadecane emulsion. The left side remains largely dry, while a film of liquid covers the right side. Credit: *Science Advances* (2022).

DOI: 10.1126/sciadv.abl7160

Outlook

The team thereby explored the effects of oil viscosity and formed a design map for effective emulsion sprays with an optimal range of viscosities and optimal Weber number range. They designed the sprays to meet the Weber number and viscosity regimes. They performed additional macroscopic experiments with the sprays and obtained high-speed videos of water and emulsion sprays impacting a superhydrophobic surface. In this way, Damak and colleagues unveiled a hitherto unknown mechanism to stick emulsion droplets on superhydrophobic surfaces. The team explored the underlying mechanisms of physics to show the efficiency of the method during spray retention with the model surfactant-free system.

Future work could be promising, with applications in agriculture already underway, as Damak explains: "The research is being translated to the market through a startup we founded, AgZen. We are developing sprayers and procedures to greatly enhance the efficiency of spraying and reduce waste in agriculture and will be doing field trials with growers soon." The scientists envision improved spray retention with minimized environmental pollution with pesticides for efficient applications.

More information: Maher Damak et al, Dynamics of an impacting emulsion droplet, *Science Advances* (2022). DOI: 10.1126/sciadv.abl7160. www.science.org/doi/10.1126/sciadv.abl7160

Thomas M. Schutzius et al, Spontaneous droplet trampolining on rigid superhydrophobic surfaces, *Nature* (2015). DOI: 10.1038/nature15738