Supporting Information

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Enhanced Condensation on Soft Materials through Bulk Lubricant Infusion

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Supplementary Information

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1. Substrate composition and Gas permeation chromatography (GPC)

| Substrate | Base: Crosslinker Ratio | Lubricant in the substrate (%) |
|-----------|------------------------|-------------------------------|
| P10L0     | 10                     | 0                             |
| P10L5     | 10                     | 5                             |
| P10L25    | 10                     | 25                            |
| P1L0      | 1                      | 0                             |
| P1L5      | 1                      | 5                             |
| P1L25     | 1                      | 25                            |
| P40L0     | 40                     | 0                             |

Table S1: Composition of all substrates

Gas permeation chromatography

GPC experiments were performed using an Agilent Technologies 1260 instrument consisting of a pump, autosampler and column oven. As eluent toluene was used. A column set consisting of 3 columns: SDV $10^6$ Å, SDV $10^4$ Å and SDV 500Å (PSS Standards Service GmbH, Mainz, Germany), all of 300 x 8 mm and 10µm average particle size were used at a flow rate of 1.0 mL/min and a column temperature of 30 °C. The injection volume was 100 µL. Detection was accomplished with a RI detector (Agilent Technologies). In order to reproduce the measurement, each sample was injected twice.

Data acquisition and evaluation was performed using PSS WINGPC UniChrom (PSS Polymer Standards Service GmbH, Mainz, Germany). Calibration was carried out by using the universal calibration method with polystyrene standards provided by PSS Polymer Standards Service GmbH (Mainz, Germany) and the Mark-Houwink coefficients for PDMS in toluene.

Figures S1 below shows result of GPC analysis for P1L0, P1L5 and P1L25. Similarly, to the discussion in main text, the lubricant contributes towards additional uncrosslinked chains in P1L5 and P1L25.
Figure S1: Molecular weight distribution of uncrosslinked chains in P1L0, P10L5, and P10L25 overlaid on the distributions for precursors

2. Energy model and dissipation ratio

As a droplet slides on the vertical surface of a soft substrate, it attains a terminal velocity $U_{drop}$ when the work done by the weight of the drop is balanced by viscous dissipation within the drop ($\dot{D}_v$) and viscoelastic dissipation within the substrate ($\dot{D}_{ve}$). Hence $mgU_{drop} = \dot{D}_v + \dot{D}_{ve}$.

| Substrate | $\theta$  | $m$ | $U_0$ (µm/s) | $V_0$ (µL) | $\frac{\dot{D}_{ve}}{\overline{D}_v}$ | $\frac{\dot{D}_{ve}}{\overline{D}_v}$ | $P10L0$ | $\frac{\dot{D}_{ve}}{\overline{D}_v}$ |
|------------|------|----|------------|----------|-------------------------------|-------------------------------|---------|-------------------------------|
| P10L0      | 90.1±3.5 | 0.23 | 13.38      | 3.96     | $1.2 \times 10^5$             | $1.2 \times 10^5$             | 1       | 1                             |
| P10L5      | 86.2±0.9  | 0.26 | 155.14     | 2.83     | 42.2                          | 27.9                         | 1       | 27.9                          |
| P10L25     | 81.8±1.1  | 0.26 | 2062.65    | 6.05     | 20.5                          | 57.4                         | 1       | 57.4                          |
| P1L0       | 79.4±2.1  | 0.49 | 171.68     | 4.73     | 133.4                         | 8.8                          | 1       | 8.8                           |
| P1L5       | 75.7±2.1  | 0.41 | 812.83     | 12.05    | 115.8                         | 10.1                         | 1       | 10.1                          |
| P1L25      | 77.8±3.4  | 0.39 | 1244.67    | 11.27    | 76.1                          | 15.4                         | 1       | 15.4                          |
| P40L0      | 91.6±7.3  | 0.08 | 0.99       | 10.1     | $3.1 \times 10^5$             | $0.003$                      | 1       | $0.003$                       |
Table S2: Fitting parameters and dissipation ratios for various substrates estimated based on droplet sliding experiment data. Dissipation ratios are calculated for droplet of volume 5µl for all substrates except P40L0 for which droplet of volume 8 µl (minimum droplet size for which sliding velocity on P40L0 could be recorded in our experiments) is used\cite{1}.

Figure S2: Droplet sliding velocities as a function of droplet volume for P1L0, P1L5 and P1L25

Here $\dot{D}_v = \frac{6\pi\mu l u_{drop}^2}{\theta}$ and $\dot{D}_{ve} = \frac{2\gamma^2 l}{\pi G h} \left( \frac{U_{drop} m+1}{u_0 m} \right)$\cite{1}. Here, $\gamma$ and $\mu$ are density and viscosity of the liquid respectively, $\theta$ is the apparent contact angle and $U_0$ and $m$ are rheological constants for a substrate. $l$ and $l$ are constants based on droplet morphology with $l = \int_0^{\pi/2} \cos^{(m+1)}(\phi) d\phi$ and $l \approx \log(1000)$, $r$ is the base radius of the drop and $h$ is the wetting ridge height \cite{1}. The volume of the drop $V_{drop}$ is calculated as $V_{drop} = r^3 f(\theta)$ with $f(\theta) = \pi(2 + \cos \theta)(1 - \cos \theta)/[3 \sin \theta(1 + \cos \theta)]$. Assuming $\dot{D}_{ve} \gg \dot{D}_v$ results in the equation $\log(U_{drop}) = \frac{1}{m} \log\left(V_{drop}^{2/3}\right) - \frac{1}{m} \log\left(\frac{2\gamma^2 l}{f^{1/3}(\theta)\pi G h u_0^m \rho g}\right)$. Fitting the experimental data to this linear relationship between $\log(U_{drop})$ and $\log\left(V_{drop}^{2/3}\right)$ yields values for $m$ and $U_0$ for a substrate. With these values known, the model fit shown in Figure 2 of main text is given by $U_{drop} = \frac{u_0}{V_{drop}^{2/3}} V_{drop}^{2/3m}$ where $V_0 = \left(\frac{2\gamma^2 l}{\pi \rho G h f^{3}(\theta)}\right)^{3/2}$. Additionally, the dissipation ratio $\frac{\dot{D}_{ve}}{\dot{D}_v}$ can be calculated for all substrates. Table S1 list the values of apparent contact angle, model fit parameters and dissipation ratio values for
various substrates. The estimated dissipation ratios show that bulk lubricant infusion in PDMS with stoichiometric monomer–to–crosslinker ratio of 10:1 results in the most reduction in viscoelastic dissipation. Additionally, comparing P1L0, P1L5 and P1L25, we find that bulk lubricant infusion in PDMS with non-stoichiometric monomer to crosslinker ratio does not lead to any significant reduction in viscoelastic dissipation. This is also evident from comparison of droplet sliding velocities for these substrates as illustrated in Figure S2.

3. Pre-coalescence droplet growth on P1L0, P1L5, P1L25 and P40L0

As shown in Figure S3(a), the comparison between pre-coalescence condensate droplet growth rates for P1L0, P1L5 and P1L25 is similar to that between P10L0, P10L5 and P10L25 shown in Fig. 4 of main text. Figure S3(b) shows pre-coalescence condensate droplet growth rate on P40L0 and also compares these rates for all the substrates considered in this work. The comparison shows that, among the PDMS substrates with bulk lubricant infusion, P10L5 and P10L25 achieve higher droplet growth rate compared to P1L5 and P1L25. Droplet growth rate on P40L0 is the lowest among all substrates.

Figure S3: (a) Pre-coalescence condensate droplet growth on P1L0, P1L5 and P1L25 (b) Comparison of pre-coalescence condensate droplet growth on all PDMS substrates

4. Experimental details to measure cloaking timescale

The experimental procedure to measure differences in timescale for cloaking of water droplets between P10L0 and P10L25 consists of following steps which were automated using the Krüss Advance software.
A syringe tip (1.8 mm outer diameter) is lowered into the hole until it is a few millimetres below the lower surface. 25 μL of MilliQ water is dosed at 3 μL s⁻¹. Subsequently, we wait for 10 s for any vibrations from the dosing to subside and then measure the surface tension while drop is hanging from the syringe tip. This is to ensure that the initial calculated surface tension of the drop, before it comes into contact with the surface, corresponds to the expected value of ≈72 mN m⁻¹. Then the syringe is moved upwards until the drop touches the surface and the drop volume is increased by 13 μL to 38 μL at 5 μL s⁻¹. 38 μL corresponds to the maximum drop volume that can be supported by a 2 mm diameter contact line, assuming that the effective surface tension of the drop decreases to ≈60 mN m⁻¹ after cloaking. The surface tension measurements are taken at a frequency of 1-10 Hz, depending on how fast the process is expected to be. At the end of the experiment, the syringe tip is pulled out of the drop and the surface tension of the pendant drop is measured (without the tip attached to it). This is to check if the presence of the syringe tip was influencing the measured surface tension. Repeated measurements on the same substrate shows variations in the cloaking timescale (Figure S5). However, cloaking always happened significant faster on P10L25.

![Figure S5: Evolution of surface tension of a water drop hanging from P10L5 (left) and P10L25 (right). The different colors on each plot correspond to repeats of the same experiment. The order of the repeats corresponds to the rainbow colors, with red corresponding to the first experiment. The time between each repeat experiment was ≈ 5 minutes. With P10L0, there is no change the measured surface tension for over 30 minutes.](image-url)
5. Determination of substrate shear modulus using micro-indentation tests

Figure S6 shows a schematic of the micro-indentation test used to measure substrate Young modulus. The micromechanical testing station FT-MTA02 (FemtoTools AG, Buchs ZH, Switzerland) consists of a micro robotic manipulation system (FT-RS1002) and a universal measurement stand with a tilt-table digital microscope (FT-UMS1002). Force sensing probes (type FT-S1000) with a range of +/-1000µN and a sensitivity of 0.05 µN were used. Spheres of cubic zirconia (Sandoz Swiss precision spheres; grade 10) with a radius \( R = 100 \) µm were glued to the silicon-tip of the sensing probe using a light curing adhesive (Loctite AA3494). A contact finding step (200 µm/s) with a corresponding force threshold (10µN) was performed before each indentation measurement. An indentation speed of 0.5µm/s was applied for all samples. For each sample 4 measurement points were recorded, forming an equidistant grid of 2x2 points on an area of 0.5 x 0.5 mm.

\[
\dot{\delta} = 0.5 \text{ µm/s}
\]

\[
\delta_{\text{max}} \quad \text{cubic zirconia sphere}
\]

\[
R = 100 \text{ µm}
\]

\[
\text{sample}
\]

**Figure S6**: Schematic overview of the sensing probe-tip, represented in the deformed state

In order to determine the Young’s modulus, a maximum indentation depth of \( \delta_{\text{max}} = 5\mu m \) (Figure S1) was considered. A Hertzian contact model \(^2)\) was used, assuming a Poisson’s ratio of \( \nu=0.5 \) (incompressible material).\(^3\) A Nelder-Mead downhill simplex algorithm in Python (binaries provided by the scipy.optimize module \(^4\)) was used to find an optimal parameter set \((\alpha, \beta)\) of the force function \( \alpha(\delta - \beta)^{3/2} \). The Young’s modulus is then given by

\[
E = \alpha \left( \frac{3}{4R^2} (1 - \nu^2) \right)
\]

For each sample the Young’s modulus was calculated for all four
locations. Subsequently these values were averaged over each sample. Substrate shear modulus was then calculated as $G = E/3$.\textsuperscript{[1]}

6. Additional data on wetting ridge height

![Graph showing wetting ridge height as a function of droplet volume for four substrates.](image)

**Figure S7:** Wetting ridge height as a function of droplet volume for four substrates. The wetting ridge height shows minimal variation for the range of droplet volumes for each substrate. However, for consistency, wetting ridge heights measured using droplets of volume ~12µL or larger were reported in Figure 1 in main text.

7. Droplet sliding experiments

Figure S8 shows a schematic of the custom made droplet sliding experiment setup which was used to characterize the substrate viscoelasticity. The sample was contained in a Petri dish and illuminated from behind with a white LED. The cured sample was ~2 mm thick. For each measurement, the droplet volume was controlled by using micropipette (Eppendorf Research) and the droplet was deposited gently on the substrate by bringing the tip of the pipette as close as possible to the substrate surface. Thus, care was taken to minimize any initial velocity effect of the droplet. Subsequently, the droplet motion was recorded as it started sliding along the
substrate, by using a scientific CMOS camera. For each droplet size, the experiment was repeated for 3 droplets and two samples of each type. The values for the velocities were computed by dividing the travelled distance of droplet centroid over the corresponding time.

**Figure S8:** Schematic of the droplet sliding experiment

8. Microscale condensation setup

**Figure S9:** Schematic of micro-condensation setup

9. Dewing experiments
Figure S10 shows a schematic of the custom-built experimental setup for dew collection. It consists of a poly (methyl methacrylate) (PMMA) chamber with interior dimensions 250 mm × 180 mm × 400 mm. A 4 mm inlet at the corner of the box allows the entry of humid air at a mean speed of 9.1 m/s (FAM3255, ABB), generated by passing compressed air through a bubbler. A copper plate, which is screwed onto a temperature-controlled Peltier stage (CP-200TT, TE TECHNOLOGY), allows three samples to be mounted vertically and tested simultaneously. An RTD is attached onto the copper plate to monitor its surface temperature. Two temperature and relative humidity sensors (SHT31, Sensirion) are placed in the box near the samples. A PMMA plate is situated between the humid air inlet and the 3 samples to reduce the effects from vortices due to the air jet. A DSLR (D7500 and AF-S DX Zoom-Nikkor 12-24mm f/4G IF-ED, Nikon) is used to monitor the condensation behaviour by taking photographs at specified intervals using its internal timer.

Figure S10: Dew collection experimental setup. A PMMA box encloses the humid air with one end open for the Peltier stage and samples. A hole is seen on the top left for incoming humid air generated by a bubbler. A plate is placed between the inlet and the samples to avoid effects from the jet affecting the flow condition at the samples. A copper plate is used to mount three samples.

Dew condensed on the samples is collected in water collection trays as shown.

The 3 PDMS samples are directly fabricated on the copper plate. 3D-printed white polycarbonate mounts are first attached to the copper plate with Kapton tape. PDMS is poured into these mounts and cured in the oven together with the mounts and the copper plate. The resulting cured PDMS samples of ~ 2 mm thickness thus have direct contact with the copper plate. Water condensed on the PDMS surfaces are collected in the trays of the mounts as they depart. For each PDMS sample, the dimensions of condensing area are 45 mm × 45 mm.
Experimental procedure: After the 3 PDMS samples are cured in the oven, they are allowed to cool in ambient air. The copper plate with the mounts and the samples is then screwed onto the Peltier. An RTD is attached onto the copper plate with Kapton tape. The Peltier stage is set to 25 °C. The temperature and humidity sensors are then placed near the samples. As humidity reaches ~ 70 %, the camera is set to capture photographs using aperture mode, at f/4 aperture and ISO 1600 at specified intervals using the internal timer, with exposure smoothing turned on. The Peltier temperature is set, resulting a copper plate surface temperature measured by the RTD of ~ 2 °C. The setup is let to run for ~ 17 hours with copper plate temperature and chamber temperature and humidity continuously monitored. After ~ 17 hours, the Peltier is switched off. The bubbler is kept running to avoid evaporation of collected water due to large drop in humidity. A cleanroom towel is used to remove water on top of the PDMS which has not departed into the tray. A surgical blade is used to remove the mount from the copper plate, with the collected water in its tray. Another cleanroom towel is used to remove water on the mount which is not in the tray. The mount is subsequently weighed. The weighing process is repeated for all 3 mounts. After that, the mounts are completely dried with nitrogen and weighed again. The difference in mass is taken as the amount of water collected for the 3 samples. Finally, the PDMS samples are removed from the copper plate and their thicknesses are measured. The experiment is repeated with the positions of the 3 samples on the copper plate shuffled to reduce effects due to the flow condition. The data reported in the main text are averages of 4 experiments.

Lubricant depletion experiment: Condensed water droplets cloaked with uncrosslinked chains can provide a mechanism of lubricant depletion when they are shed from the surface.\cite{Schellenberger2007} Schellenberger et al.\cite{Schellenberger2007} have estimated that for lubricants that can cloak water droplets, a cloaking layer of ~ 20 nm is formed on the drop. Considering water drops that shed from surface to be of the order of 1 mm in radius, this cloaking layer thickness estimate translates to the lubricant volume per water drop to be about $10^5$ times smaller than droplet volume. Hourlier-Fargette et al.\cite{Hourlier-Fargette2019} have also reported similar estimate for the lubricant volume lost per drop for PDMS P10L0. Thus lubricant depletion from the substrate through dewing is likely to be small.

We have verified the lubricant loss from the substrate through an extended dewing experiment. Since the cloaking layer thickness is governed by a balance between capillary
pressure due to curvature in the cloaking film and disjoining pressure,[6] we expect that thickness of oil layer on cloaked droplets will be similar between P10L0, P10L5 and P10L25. Moreover, we have already shown that cloaking is faster on P10L25 and P10L5 compared on P10L0. Thus we have selected P10L25 for the additional dewing experiment to test the durability of these substrates for lubricant depletion over time. The details of this experiment are described below:

We first measure the initial mass of three P10L25 surfaces and then exposed them to dewing in the same setup used for the previous dewing experiments for the same duration (17 h). Upon drying with nitrogen, no measurable change in mass was detected. The samples were then further exposed to dewing for 94.6 h. Thus the total time for exposure to dewing conditions was 111.6 h. The samples were then dried with nitrogen and left open to atmosphere for 3 more days for any possibly absorbed water to evaporate and leave the sample. Compared to the initial mass before any condensation experiments, the mean decrease in the final mass of the samples on the last day is ~1 mg. Given a mean initial sample mass of 3528 mg, the mean initial lubricant mass (25 wt. %) was 882 mg. Assuming that the reduction in sample mass is mainly due to lubricant loss, the lubricant loss over 111.6 h was ~0.11%. We conclude that this lubricant loss is negligible. Additionally, this also means an average lubricant loss rate of 4.6 µL/m²h. Comparing with the dewing rate of 43 mL/m²h on P10L25 (see Figure 7 in main manuscript), we reach an estimate for average rate of lubricant addition in water of ~0.011% per hour by volume of water condensed on the substrate.

Comparison of dew water collection and droplet departure diameters on PDMS substrate and a rigid hydrophobic substrate: We compare dewing on PDMS substrate against a rigid hydrophobic substrate. For this comparison, we choose P10L0, which has the highest shear modulus among all PDMS substrates (see Figure 1) and a hydrophobic planar copper surface. PDMS substrate has a much lower thermal conductivity,[7,8] and hence a higher thermal resistance, compared to metals. Thus, the dewing performance of P10L0 and hydrophobic copper substrate is compared at similar level of surface subcooling.[9]

45 mm x 45 mm x 2 mm Cu-DHP plates are used as the substrate to prepare hydrophobic rigid samples. The substrates are first wiped with acetone, and then sonicated in HCl (37%) for 10 minutes. They are then immersed and sonicated in deionized water for 10 minutes. Further
cleaning is performed by sonicating the samples in acetone, isopropanol and deionized water each for 10 minutes. They are then dried with nitrogen. In a nitrogen environment, 22.88 µL of warm 1H,1H,2H,2H-Perfluorodecanethiol (Sigma-Aldrich) is added to 80 mL of warm ethanol and mixed. The solution is sonicated for 5 minutes, and the substrates are placed into the solution for 1 hour. The samples are rinsed with ethanol and dried with nitrogen, followed by heating at 80 °C for 30 seconds.\textsuperscript{[10]} The samples are let to cool down in ambient and confirmed to be hydrophobic with droplets of deionized water.

For the dewing experiment on the two substrates at same subcooling, first, three P10L0 samples are prepared and an RTD is attached on top of one of the samples. These samples are exposed to similar dewing conditions as the water collection experiments corresponding to Figure 7 in main text, to obtain an estimation of the surface temperature of PDMS samples (~6.2 °C). Subsequently, three hydrophobic planar Copper samples are tested under the same dewing conditions. An RTD is attached to one of the Copper samples and the same surface temperature as that for P10L0 is then targeted by adjusting the Peltier cooling stage set point. Once the stage temperature is set such that the surface of the copper reaches the target temperature, the setup is let to run for a total of 17 hours without further intervention. In these two experiments, the atmospheric relative humidity was ~ 60% and air temperature was ~19°C. Under these conditions, average dew collection rate of 51.3 mL/m\textsuperscript{2}h and 23.8 mL/m\textsuperscript{2}h is measured on P10L0 and hydrophobic copper respectively. While the droplet shedding onsets after about 2.4 hours on P10L0, it takes more than 8 hours on hydrophobic Copper substrate for onset of droplet shedding.

Figure 11 compares condensate droplet departure diameters on P10L0, P10L5 and P10L25 with rigid hydrophobic copper substrate. These diameters have been determined by considering 35, 37, 94 and 109 droplet departure events on hydrophobic copper, P10L0, P10L5 and P10L25
Figure 11: Comparison of condensate droplet size departing from the substrate during dew water collection

respectively. The droplet departure diameter on planar hydrophobic copper is larger than all the PDMS substrates. The contact angle hysteresis on P10L0 is measured to be $\sim 38^\circ$, much lower than $\sim 94^\circ$ on planar hydrophobic Copper substrate,$^{[10]}$ The higher contact angle hysteresis, along with inherently lower nucleation density on rigid substrate, leads to lower dew water collection on hydrophobic copper.

10. Supplementary video

Supplementary video shows condensation on P10L0, P10L5 and P10L25 atmospheric relative humidity of 68.6%, air temperature of 16.6 °C and copper plate surface temperature of 2.1°C (mean conditions across four experiments).

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