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1 **Title:**

2 **Thin adhesive oil films lead to anomalously stable mixtures of water in oil**

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15
16 **Abstract:**

17 **Oil and water can only be mixed by making droplets of one fluid in the other. When two droplets approach**
18 **one another, the thin film that separates them invariably becomes unstable, causing the droplets to coalesce. The**
19 **only known way to avoid this instability is through addition of a third component, typically a surfactant, which**
20 **stabilizes the thin film at its equilibrium thickness. We report the observation that a thin fluid film of oil separating**
21 **two water droplets can lead to an adhesive interaction between the droplets. Moreover, this interaction prevents**
22 **their coalescence over time scales of several weeks, without the use of any surfactant or solvent.**

23
24 **One-Sentence Summary: Adsorption of polymeric oil on a water interface leads to weak adhesion and**
25 **metastability for emulsion droplets**

26
27
28 **Main Text:**

29 Oil and water do not mix. When the two are violently shaken together, droplets of one fluid will form inside the
30 other, but when two droplets are brought in close proximity to one another they are unstable and coalesce to form a single
31 droplet. As the interfaces approach one another, the intervening fluid layer becomes very thin and thermally induced
32 capillary waves on each interface lead to merging (1). This can only be avoided through the addition of a third component,
33 a surfactant, which induces a repulsive interaction that prevents spontaneous coalescence due to capillary waves, except in
34 highly specific cases such as water-in-liquid-crystal emulsions (2), some very dilute charged systems (3) or when some
35 intrinsic impurities can act as surfactant (4). Instead, coalescence can only occur in the thin fluid film separating the droplets
36 through a thermally activated nucleation of a hole that must reach a critical size above which it becomes unstable (5). The
37 activation energy for nucleation of a hole can be large, leading to long term stability of the surfactant stabilized droplets. In
38 some cases there can be an attractive interaction which causes droplets to adhere to one another while still retaining their
39 integrity due to the adsorbed surfactant (6). For example, a classic observation is when oil droplets in water, commonly
40 called direct emulsions, are stabilized by a widely used surfactant such as SDS (sodium dodecyl sulfate). The addition of
41 excess salt causes interfaces of neighboring droplets to wet one another resulting in a very thin water film separating the

droplets (7). This leads to adhesion but the stability of the droplets is retained. Similar behavior can be observed for water droplets in oils, commonly called inverse emulsions: Addition of a solvent to the oil can cause the surfactant stabilizing the droplets to become less soluble in the continuous phase, and hence induce an attractive interaction which leads the droplets to wet one another; nevertheless coalescence is still avoided due to the surfactant (8, 9). Attractive interactions between droplets can only occur when molecules at the interface of the droplets are more compatible with one another than with the solvent itself. In all cases stability of a thin oil film separating two water droplets can only be achieved through the incorporation of one or more additional components able to adsorb at the interfaces (10).

We report the spontaneous formation of an anomalously stable thin film of oil between droplets of water for a polymeric oil. When there is weak adsorption of the oil on the water interface, the oil molecules at the interface become less compatible with the bulk oil, resulting in a weak attractive interaction between the two water droplets which induces a dramatic change in the dynamics of the oil molecules within the thin film. As a result, the water droplets can remain stable over large time scales, even in the absence of surfactant or any other additional components whatsoever. By measuring the temperature dependence of this stability, we show that it results from an increase, by seven orders of magnitude, in the effective viscosity of the oil in the thin adhesive films between the droplets, as compared to the bulk viscosity. As a consequence, stable water-in-oil emulsions can be produced in the absence of surfactant even at very high volume fractions of water. Moreover, because of this unexpected metastability, above a characteristic water volume fraction, ϕ^* , the emulsion breaks under shear and spontaneously forms double emulsion globules comprised of the primary water-in-oil dispersion.

Adhesion of stable oil films separating water interfaces.

To illustrate this phenomenology, we investigate the behavior of a pure binary mixture of glycerol and polydimethylsiloxane (PDMS) (**fig S1**). We mix glycerol ($\eta_g = 0.84$ Pa.s) into PDMS oil ($M_w = 30\,000$ g/mol) (11) with a viscosity of $\eta_0 = 1$ Pa.s to form glycerol droplets of diameter D of about $2\ \mu\text{m}$ (Methods 1). As the droplets approach one another, instead of coalescing, they stick to each other while still retaining their integrity (**Fig 1A**). The existence of these compact clusters indicates that there must be an adhesive interaction between droplets. To confirm this, we use micropipette aspiration to immobilize a doublet comprised of one droplet adhering to a second (Methods 2). The two droplets adhere to one another, demonstrating the attractive interaction, as shown in **Fig. 1B**. To measure this attractive interaction, we illuminate the interface between two droplets with a laser and analyze the resultant interference pattern (12). The adhesive patch causes a black central circle in the interference pattern, as seen in **Fig. 1C**. The size of this circle enables us to determine the diameter of the adhesive patch (7), a , from which we deduce the contact angle of the adhesive droplets, θ , which we find to be $\theta = 2^\circ$ (Methods 3 and **S**) (13). By determining the surface tension between glycerol and PDMS, $\gamma = 25$ mJ/m², we can determine the adhesive energy (14), $\varepsilon = 2\gamma(1 - \cos\theta)$, which gives $\varepsilon = 3 \times 10^{-2}$ mJ/m². For two identical droplets, if $\varepsilon/\gamma \ll 1$, the diameter of the adhesive patch must scale with the diameter of the drop as (6) $(a/D)^2 = \varepsilon/\gamma$. Although the area of each adhesive patch is very small, coalescence must take place within the patches since the contact angle leads to further separation of neighboring interfaces.

78

79 **Origin of the stability of the thin oil films**

80 To quantify the stability of these thin adhesive oil films, we measure the time evolution of the size distribution of
 81 droplets due to coalescence which is the dominant mechanism of coarsening (**movie S1**). We use an emulsion with a volume
 82 fraction, $\phi = 76\%$, which is high enough to preclude any significant relative motion of the droplets, ensuring that the
 83 measured coalescence rate reflects only the intrinsic instability of the thin films separating droplets in contact with one
 84 another (15). We determine the number-averaged size distribution (Methods 4). It maintains a constant shape while the
 85 mean size increases with time, as shown in **Fig. 2A**. To probe the nature of the metastability of the thin oil film, we measure
 86 the temperature dependence of the evolution of the mean diameter: For each temperature, T , the initial time dependence of
 87 D is linear, while the rate of growth increases markedly with increasing T , as shown in **Fig. 2B**. The frequency of
 88 coalescence, ω , is proportional to the rate of growth normalized by the initial drop diameter. We find that $\log \omega$ depends
 89 linearly on the inverse of T , as shown in **Fig. 2C**. Thus, the coarsening exhibits an Arrhenius behavior given by $\omega =$
 90 $\omega_0 e^{-E_a/k_B T}$, where ω_0 is the attempt frequency, k_B is Boltzmann's constant, and E_a is the energy barrier for the nucleation
 91 of a hole, of critical radius, r^* , in the thin film separating two droplets, which induces coalescence. From the slope of the
 92 data, we determine $E_a = 20 k_B T$, with $T = 298$ K. By comparison, surfactant stabilized emulsions typically exhibit a
 93 significantly higher energy barrier of at least $30 k_B T$ (16).

94 To determine the value of r^* , we use the simplest model of nucleation and growth, the capillary model (17). The
 95 energy, $E(r)$, of a hole of radius, r , is $E(r) = -2\pi r^2 \gamma + 2\pi r \Gamma$, where γ is the surface tension and Γ is the line tension which
 96 accounts for all contributions associated with the inherent high curvature along the perimeter of the hole (**S**). This leads to
 97 $r^* = \left(\frac{E_a}{2\pi\gamma}\right)^{1/2}$, and we obtain $2r^* = 1.4$ nm. From this value, we can also infer the thickness of the film, h , which, as
 98 assumed by the capillary model, must be of the same order of magnitude, a few nm (18).

99 Further insight into the nature of this behavior comes from determining the attempt frequency, $\omega_0 \sim 10^5 \text{ s}^{-1}$, which
 100 is obtained from the intercept of the fit to the data in **Fig. 2C**. The nucleation rate of a hole (19), k_0 , is determined by a
 101 balance between surface tension, which drives the growth of the hole, and the viscosity of the oil in the film, which slows
 102 the growth, $k_0 \sim \frac{\gamma}{\eta r^*}$. The value of ω_0 is determined by k_0 normalized by the number of holes possible, $\omega_0 = k_0 \frac{s}{r^{*2}}$, where
 103 s is the specific surface area of one drop in contact with its neighboring droplets, where coalescence must occur. Each drop
 104 is surrounded on average by a number, z , of neighboring droplets. Therefore, the fraction of the drop surface occupied by
 105 adhesive patches is $z\left(\frac{a}{D}\right)^2$, which is about 1% of the drop surface if we assume $z = 10$, as expected for a densely packed
 106 emulsion. Thus, within the thin adhesive film, the effective viscosity of the oil, η_{eff} , must be a factor of $\sim 10^7$ more than
 107 η_0 (**fig. S2**). It is this large increase in the viscosity in the thin film where coalescence takes place that compensates for the
 108 relatively low activation energy and leads to this stable thin adhesive film. The uncertainty of this estimate is about an order
 109 of magnitude, given the uncertainty in the determination of ω_0 and k_0 .

110

111 **Molecular nature of the thin oil films**

112 We must therefore consider the nature of this thin adhesive film more carefully. A PDMS molecule at a hydrophilic
113 interface spreads and forms a nm-thick layer (20, 21). The preferential adsorption of the oxygen along the PDMS backbone
114 leads to an excess of hydrophilicity at the glycerol interface; this must be compensated by an excess of hydrophobicity
115 localized on the opposite side, as shown schematically in **Fig. 3A**. Thus, two identical mirror-image layers will weakly
116 adhere to one another instead of remaining surrounded by bulk oil molecules. For a glycerol-PDMS interface in contact
117 with its mirror-image, the whole film tension is lowered by $\varepsilon/2$, which is much smaller than γ . While this energy is
118 relatively small, we hypothesize that it nevertheless creates patches within which the molecular dynamics are severely
119 impacted leading to the very large increase in effective viscosity. Van der Waals interactions could also contribute to the
120 adhesion energy that we measure, however the persistence of the thin adhesive film reflects the existence of a short range
121 repulsion which must be set solely by an interplay between chain adsorption and adhesion of hydrophobic moieties (**S**).
122 Moreover, because this mechanism is molecular in scale, the thickness of these thin films must also be molecular in scale
123 in agreement with measurement on a single interface, and in accord with the value deduced by the capillary model (17, 18).

124 To explore the molecular basis of this hypothesis, we perform Nuclear Magnetic Resonance (^1H NMR)
125 measurements on concentrated glycerol-PDMS emulsions with ϕ between 60% and 76% (Methods 5). We focus on the
126 spin-spin relaxation time (T_2) of the PDMS, which reflects its molecular motion (22). For the most concentrated emulsion,
127 $\phi = 76\%$, we observe a pronounced peak, P_1 , in the T_2 relaxation time distribution centered around 9×10^{-3} s, which is a
128 factor of 14 less than the peak, P_0 , for the same PDMS in the absence of any glycerol. There is, in addition, a second peak,
129 P_2 , which appears as a shoulder around 5×10^{-2} s, as shown in **Fig. 3B**. When the volume fraction is decreased to $\phi =$
130 60%, P_1 has a smaller amplitude but remains at nearly the same position, while P_2 becomes more pronounced and shifts
131 towards P_0 , as shown in **Fig. 3B**.

132 To account for these NMR results, we hypothesize that there are two types of PDMS molecules within the
133 concentrated emulsion: one type has slow dynamics, and thus short T_2 , which is nearly independent of ϕ , as shown by the
134 position of P_1 , which remains approximately constant as ϕ changes. The other type has faster dynamics and thus longer T_2 ,
135 but does change with ϕ . We hypothesize that the first type represents PDMS molecules that are located in the direct vicinity
136 of the thin adhesive film separating droplets, while the second type represents PDMS molecules that are located in the
137 Plateau borders and includes both the molecules within the pore and those adsorbed on the pore surface but not in direct
138 vicinity of the adhesive patches, as depicted in **Fig. 3C**. Since the average dynamics of molecules within a pore includes
139 contributions from both the oil molecules adsorbed on the glycerol interface, and the oil molecules confined within the pore,
140 the peak position should change with ϕ as the relative amount of PDMS adsorbed to the interface changes as the pore size
141 changes; this is indeed what we observe for P_2 , consistent with our hypothesis. By contrast, the dynamics of the PDMS
142 molecules in the vicinity of the thin adhesive film includes contributions from those molecules confined within adhesive
143 patch itself and some molecules in close proximity to it. The structure and size of these thin films are preserved by the
144 adhesive forces, independent of dilution. Therefore, the position of the P_1 peak, which is associated with them, should not
145 change with ϕ . However, its amplitude should decay since the proportion of thin films decreases as ϕ decreases. This is
146 indeed what we observe for P_1 , consistent with our hypothesis (**S**). For the highest volume fraction, $\phi = 76\%$, the T_2 value
147 of P_1 corresponds to an effective viscosity (23) $\eta_{\text{eff}} \approx 10^4 \eta_0$; this must reflect contributions of the strongly adhesive

148 molecules directly in the film itself and the neighboring molecules whose motion is restricted but not as strongly. Thus,
149 these molecular-scale NMR results exhibit a trend that is consistent with the large increase in η_{eff} determined from the
150 analysis of the hole nucleation attempt frequency.

152 **Evidence of a generic metastability mechanism**

153 The observation of stable oil films extends beyond this PDMS oil. We produce emulsions with several different oils
154 and hydrophilic phases; each emulsion remains stable. For the aqueous phase we use either glycerol or water with the
155 addition of a few percent sodium alginate to match the oil viscosity to optimize emulsification. For each combination, we
156 measure the characteristic water volume fraction, at which the emulsion breaks under shear and spontaneously forms double
157 emulsion globules comprised of the primary water-in-oil dispersion. This provides a convenient comparison among different
158 fluid pairs. In all cases, ϕ^* depends only on the specific choice of the fluids, and not on how they are mixed. Moreover, in
159 all cases, after dilution, we observe clusters reflecting an attractive interaction between the droplets.

160 We first compare the behavior of hydroxy-terminated PDMS of the same molecular weight to that of the methyl-
161 terminated PDMS oil. Although this is a very slight modification in the molecular structure, which corresponds to the
162 replacement of only two methyl groups out of approximately 600, it nevertheless induces a large change in ϕ^* : highly-
163 packed emulsions remain stable at even higher volume fractions, up to $\phi^* = 95\%$, as shown in **Fig. 4A**. Upon dilution, we
164 observe the presence of large and dense clusters, which reflects an even stronger adhesive interaction, as seen in **Fig. 4B**.
165 Above ϕ^* the emulsion breaks under shear into a double emulsion comprised of globules with an internal glycerol volume
166 fraction $\phi_{\text{int}} = 86\%$ (Methods 6), and with somewhat larger water droplets, as shown in **Fig. 4C**. We also make stable
167 emulsions using acrylated vegetable oils; a fluorescent image of such an emulsion with $\phi = 70\%$ is shown in **Fig. 4D**. By
168 contrast to the PDMS oils, these emulsions have a lower $\phi^* = 71\%$. Upon dilution, we observe much smaller clusters
169 reflecting a weaker adhesive interaction between interfaces, as seen in **Fig. 4E**. Above ϕ^* , the emulsion breaks into a double
170 emulsion comprised of globules with significantly larger water droplets, as shown in **Fig. 4F**. This acrylated oil has a
171 polymeric backbone (**fig. S3**) which should lead to weaker adsorption and hence lower adhesion, consistent with the smaller
172 clusters observed upon dilution. We summarize the values of ϕ^* and ϕ_{int} , for PDMS, hydroxy PDMS, acrylated vegetable
173 oil and polyester oil in **Fig. 4G**. Further exploration of which oils make stable inverse emulsions with either pure water,
174 water with sodium alginate or glycerol shows that (i) silicone oil and all its derivatives including amine and phenyl
175 substituted chains produce stable emulsions, provided that oil has a polymeric character with a molecular weight exceeding
176 about 5000 g/mol (ii) polyurethane and polyester oils including their derivatives exhibit also stable water-in-oil emulsions
177 (**fig. S3**).

178
179 These findings demonstrate the unexpected behavior of a polymeric oil when it adsorbs on the interface of a
180 hydrophilic liquid and becomes confined in a very thin film. An inherent consequence of this weak binding of polymeric
181 oils to the water interface, due to their slightly polar nature, is their conformational change, exposing a more hydrophobic
182 portion of the molecule towards the bulk oil. This results in a weak adhesion between two identical interfaces and leads to
183 a dramatic increase in the effective viscosity of the oil in the thin film as compared to its bulk value; such an effect has been

184 observed so far only on a solid surface (24, 25). In the case of a liquid interface it must be understood as an intrinsic
185 consequence of both adsorption and adhesion which together efficiently modify the polymer dynamics at liquid interfaces,
186 as a direct consequence of the counterintuitive lowering of their interfacial free energy.

188 **Conclusions**

189 These results represent a mechanism for stabilizing water droplets in oil in the absence of surfactant. They also
190 represent an important route to formulate materials through double emulsions made in a single step (26, 27). When ϕ
191 exceeds ϕ^* , the emulsion breaks under shear forming a double emulsion without the use of any surfactant nor any solvent
192 whatsoever. This will have important technological applications: it enables the creation of very pure and controlled
193 materials, particularly for polymerizable oils such as those used here.

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277 **Author contributions**

278 Conceptualization: CN, DD, JW, NB, JBa, JBi

279 Methodology: CN, NB, JBa, JBi

280 Investigation: CN, AC, YS, AS

281 Visualization: CN, AC, YS, NB, JBa, DAW, JBi

282 Writing – original draft: CN, JBa, JBi

283 Writing – review & editing: CN, NB, JBa, DAW, JBi,
284

285 **Competing interests**

286 CN, DD, JBa and JBi hold patents related to this work (European unexamined patent application EP22305808 and French
287 unexamined patent application FR2306227).

288 DAW and JBi are co-founders and shareholders of Calyxia.

289 DAW and JBi have advisory activities for Calyxia.

290

291 **Data and materials availability:**

292 All data are available in the main text or the supplementary materials.

293 **List of supplementary materials**

294 Materials and Methods

295 Supplementary Text

296 Fig. S1, S2, S3

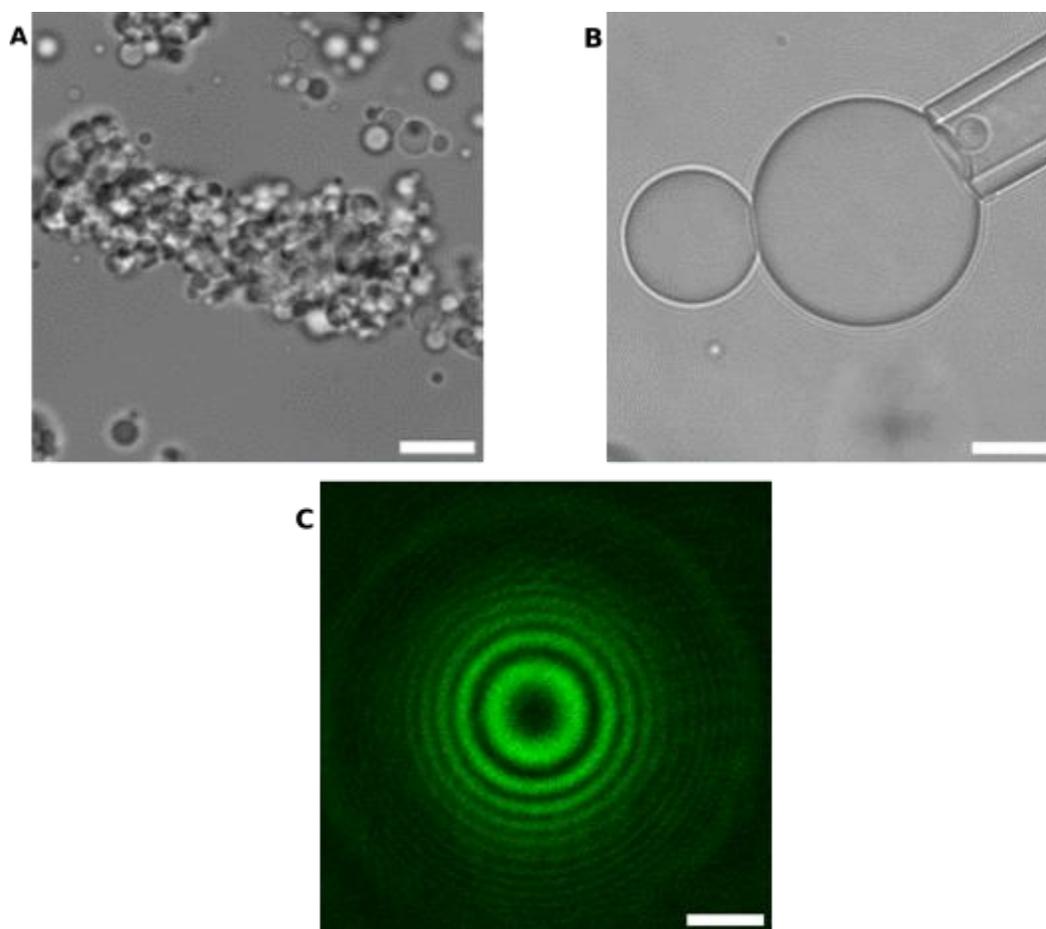
297 Movie S1

298 References (28–35)

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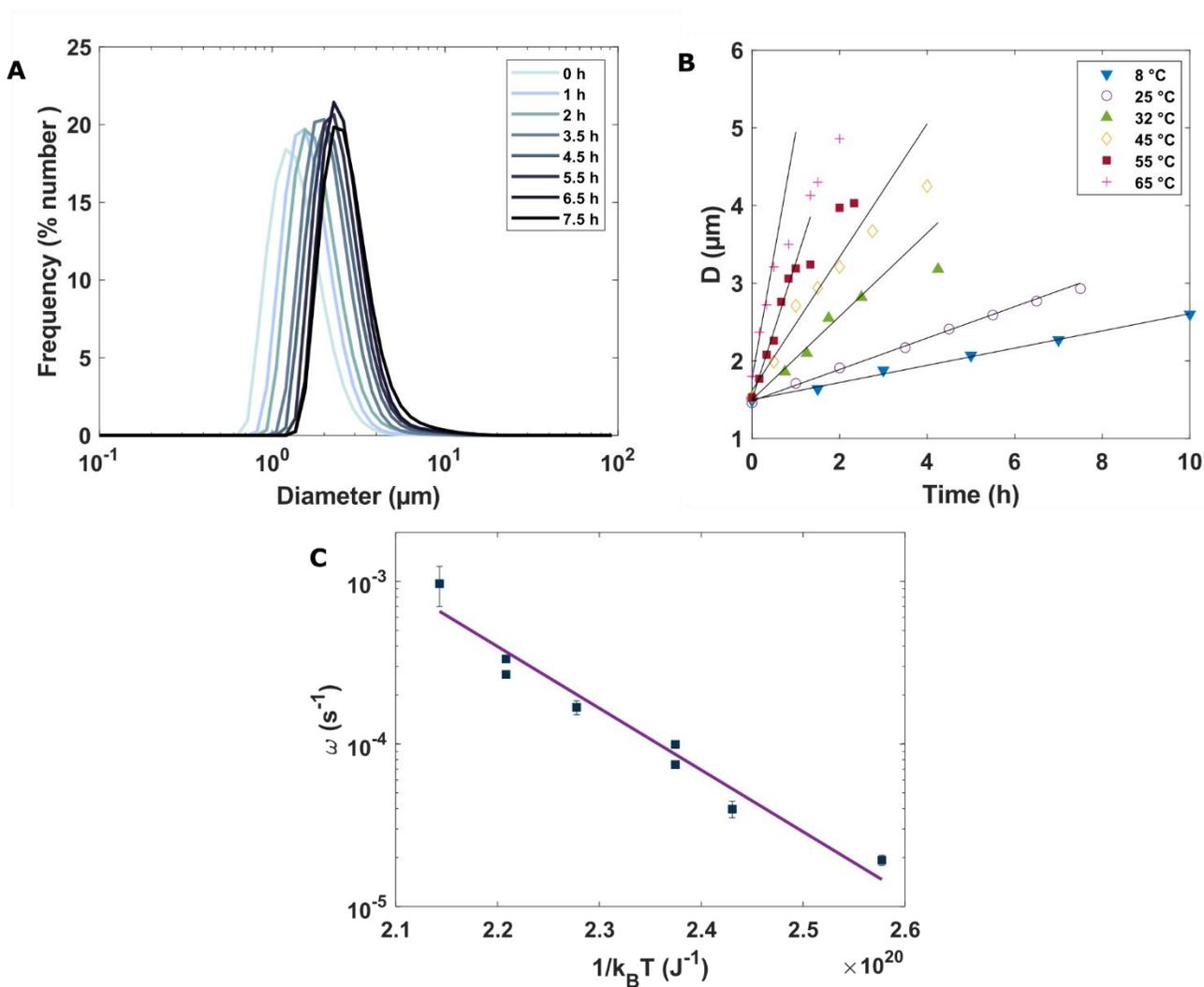
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311

Fig. 1. Adhesion in glycerol/PDMS emulsion. (A) Large stable and compact clusters of droplets: evidence of adhesion between droplets. Scale bar is 10 μm . (B) Capture of a doublet comprised of two adhesive droplets using a micropipette aspiration. Scale bar is 10 μm . (C) Transverse imaging of the oil film separating the adhesive droplets: the thin black film (central dark fringe) gives the size of the adhesive patch formed between two droplets of about 50 μm diameter. Scale bar is 2 μm .

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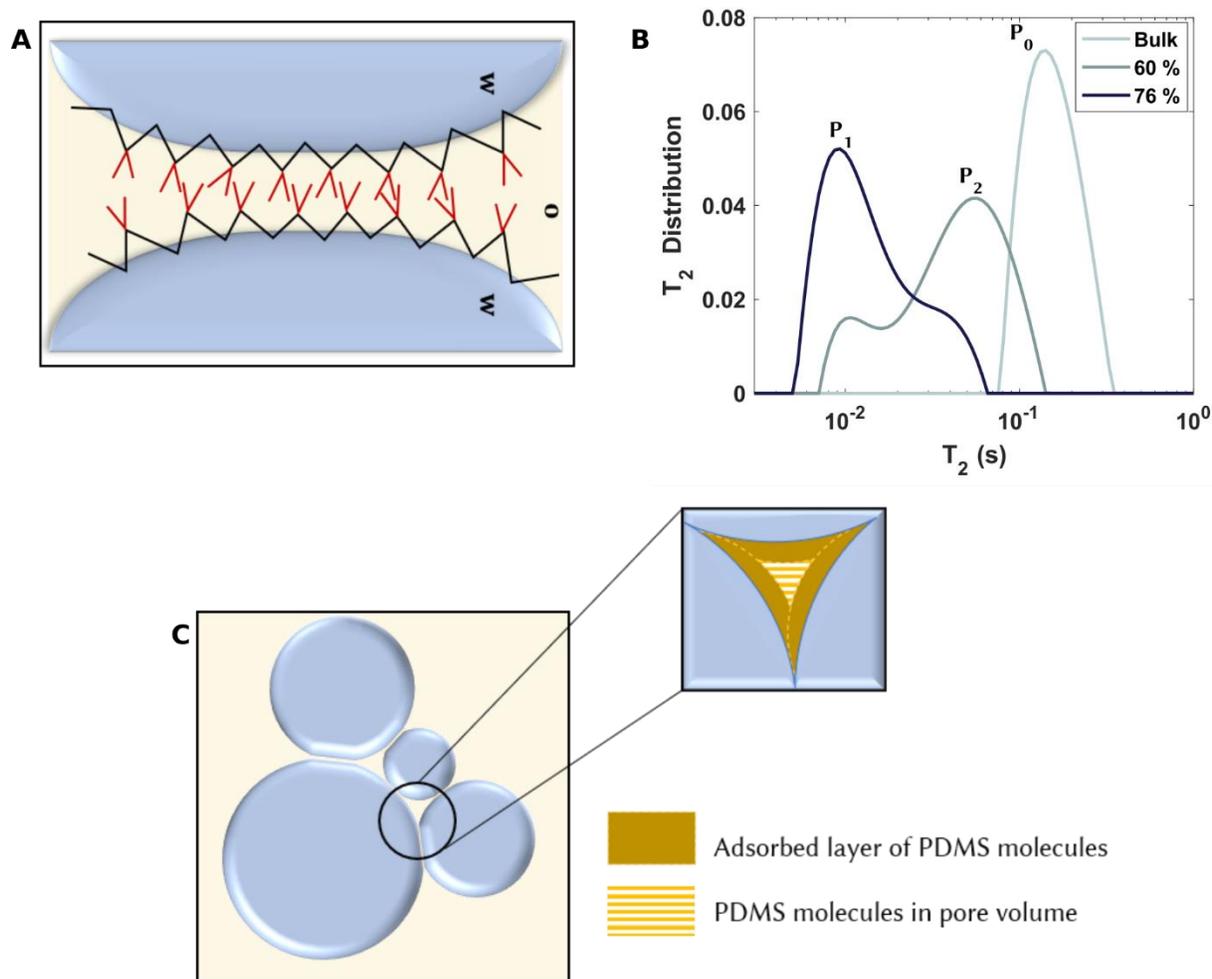
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315 **Fig. 2. Coarsening of a concentrated glycerol/PDMS oil emulsion.** (A) Droplet size distribution of a glycerol in PDMS
 316 oil emulsion at a volume fraction $\phi = 76\%$, as a function of time upon storage at 25°C . (B) Droplet mean diameter as a
 317 function of time under different storage temperatures. (C) Arrhenius plot: ω as a function of $1/k_B T$ (error bars are specified
 318 for $N=3$).
 319

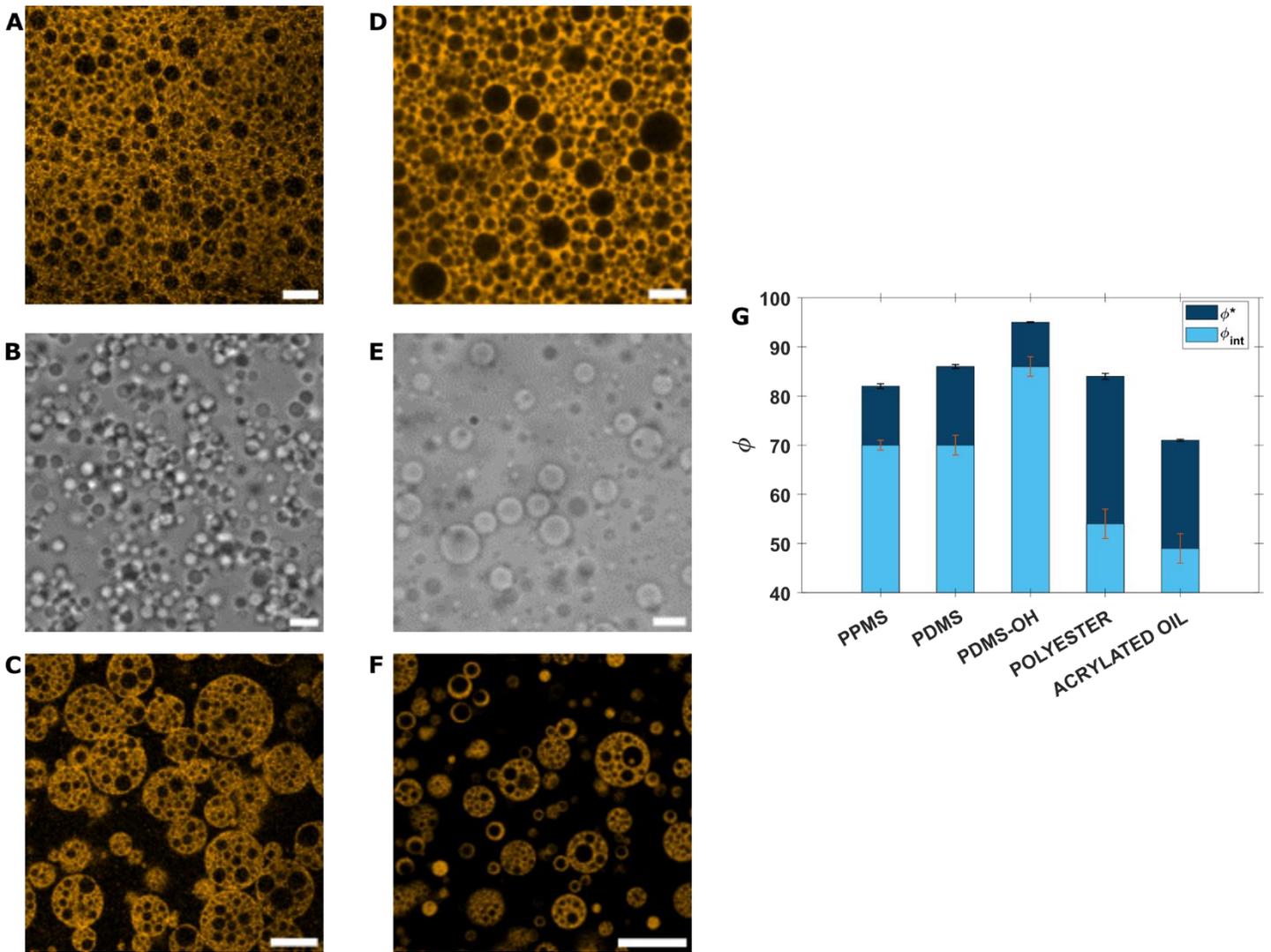
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323 **Fig. 3. Specific adsorption of oil molecules at the interface.** (A) Schematic representation of the interaction mechanism
 324 between PDMS oil/glycerol interfaces: the hydrophobic moieties of the oil (methyl group in red) specifically adhere while
 325 the hydrophilic parts of the backbone composed of oxygen atoms are preferentially adsorbed on the glycerol surface, this
 326 may account for the attraction between the droplets. (B) Plot of T_2 relaxation time distribution as a function of time for
 327 PDMS used as the continuous phase of a glycerol/PDMS oil emulsion compared to its bulk value. The bimodal T_2
 328 distribution indicates that within the emulsion, PDMS molecules are of two types: one is confined in the thin film, the other
 329 is trapped in the Plateau borders of the emulsion. (C) Schematic representation of the pore surrounded by droplets, the so-
 330 called Plateau border: the PDMS contained in Plateau borders is either located in the adsorbed layer or confined in this pore
 331 volume.
 332

333



334
 335 **Fig. 4. Emulsions formed with different oils without surfactants.** (A) A stable emulsion of glycerol in hydroxy-
 336 terminated PDMS oil (dyed orange) can be prepared at higher ϕ of 80%. Scale bar is 5 μm . (B) Microscopic picture of a
 337 diluted glycerol in hydroxy-terminated PDMS oil emulsion: evidence for compact connected clusters. Scale bar is 5 μm .
 338 (C) Double emulsion obtained with the hydroxy-terminated PDMS oil after phase inversion at $\phi^* = 95\%$. Scale bar is 10
 339 μm . (D) A stable emulsion of glycerol in acrylated vegetable oil (dyed orange) can be prepared at ϕ of 70%. Scale bar is 5
 340 μm . (E) Adhesion is also evidenced in a diluted glycerol in acrylated vegetable oil emulsion. Scale bar is 5 μm . (F) Double
 341 emulsion obtained with the acrylated vegetable oil after phase inversion at $\phi^* = 71\%$. Globules are less concentrated in
 342 internal phase as $\phi_{int} = 49\%$. Scale bar is 10 μm . (G) Critical volume fraction ϕ^* at which inversion takes place and internal
 343 fraction of glycerol within double globule ϕ_{int} ; both fractions depend on the chosen water/oil couple only (N=3, Methods
 344 5).
 345
 346
 347

Supplementary Materials for

Thin adhesive oil films lead to anomalously stable mixtures of water in oil

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The PDF file includes:

Materials and Methods

Supplementary Text

Figs. S1 to S3

Other Supplementary Materials for this manuscript include the following:

Movie S1

371 **Materials and Methods**

373 Materials

374 The following chemicals were purchased from Sigma-Aldrich and were used as received: glycerol (G7757, viscosity ~840
375 mPa.s) PDMS (polydimethylsiloxane) oil methyl-terminated (378399, viscosity~ 1,000 mPa.s and 378372, viscosity ~350
376 mPa.s), PDMS oil hydroxy-terminated (481963, viscosity ~750 mPa.s), PPMS (polyphenylmethylsiloxane) oil (10842, AP
377 1000 viscosity ~1,000 mPa.s), hexadecane (H6703), anisole (123226), Nile Red (72485), PVA (polyvinyl alcohol,
378 363170, $M_w \sim 13,000 - 23,000$ g/mol, 87 – 89% hydrolyzed). Polyester (Priolube 1847) was purchased from Croda.
379 Soybean epoxidized acrylated oil (Genomer 2312) was purchased from Rahn. Silube J208-812 was received from Siltech.
380 The acrylated oil was diluted at 83% in anisole in order to lower its viscosity.

381 Interfacial tension measurements were made using the pendant drop method (Kruss DSA30 tensiometer). The
382 glycerol/methyl terminated PDMS oil interfacial tension was measured to be 25 mN/m.

384 Methods 1: Emulsion fabrication

385 For emulsion fabrication, glassware was first cleaned using detergent and then rinsed thoroughly using ethanol and DI water
386 (Milli-Q water, Millipore).

387 To formulate the emulsions, the aqueous and oil phases were sheared using an overhead stirrer (IKA Eurostar 40) equipped
388 with a 4-bladed helix propeller (IKA, R 1342, 50 mm diameter) rotating at 1000 RPM. Emulsions were prepared in a glass
389 beaker (VWR, 213-1172, 55 mm internal diameter) immersed in a water bath to maintain a temperature around 25°C. The
390 aqueous phase was added dropwise into the oil phase using a syringe pump (Harvard Apparatus PHD Ultra) set at 25 mL/hr
391 to concentrate the emulsion until desired internal phase volume fraction ϕ was reached. The typical total volume of the
392 prepared emulsions was about 10 mL. Nile Red was mixed with the oil phase for fluorescence microscopy observations.

393 Bright-field microscopy images of the emulsions were obtained using a Nikon Eclipse E600 microscope equipped with a
394 Hamamatsu Orca-R2 camera. Confocal laser scanning microscopy images were obtained using a Nikon Eclipse Ti-E
395 microscope equipped with a Nikon D-Eclipse C1si controller, a 540 nm laser and an appropriate TRITC filter.

397 Methods 2: Micropipette aspiration

398 A crude emulsion was prepared by gently mixing glycerol in methyl terminated PDMS oil (350 mPa.s). The emulsion was
399 then further diluted at $\phi \approx 10\%$ and introduced inside an observation chamber made with two coverslips (VWR, 16004-
400 302) sandwiching a 1 mm silicone spacer (Invitrogen, P24744) which is cut on one side to allow the insertion of the
401 micropipette. A glass capillary (World Precision Instrument 1B100-6, outer diameter 1 mm, inner diameter 0.58 mm) was
402 pulled using a Micropipette Puller (P97, Sutter Instrument Company) and cut into a 10 μm tip using a microforge (MF830,

403 Narishige). The capillary was filled with the oil phase and connected to a pressure controller system with a negative pressure
404 range of 0 – ~25 mbar (Fluigent). A duet of adhesive droplets was then captured using the micropipette.

406 Methods 3: Contact angle determination

407 Contact angle determination was made through imaging of the oil film separating two adhesive droplets of diameter D_1 and
408 D_2 captured following the micropipette aspiration technique presented in Methods 2. The oil film was imaged in the
409 transverse direction using a confocal microscope (Leica SP5) equipped with a 488 nm laser and a RT 30/70 filter to obtain
410 the interference profile of the thin film. The dark central fringe corresponds to the adhesive patch of diameter a .
411 Measurement of a was performed under ImageJ image analysis software using an intensity profile. The contact angle can
412 then be determined from the following equation (13): $2\theta = \sin^{-1}\left(\frac{a}{D_1}\right) + \sin^{-1}\left(\frac{a}{D_2}\right)$. For such small contact angles, this
413 approach is much more precise than a direct measurement made by imaging a profile view of two drops where the adhesive
414 patch is perpendicular to the plane of focus.

416 Methods 4: Droplet size distribution

417 Droplet size distributions of the emulsion were measured through static light scattering (SLS) using a Malvern Mastersizer
418 3000. A few μL of emulsions was diluted in hexadecane containing 1% Silube J208-812 as surfactant to perform the
419 measurement.

420 Temperature-dependent measurements were obtained by storing the prepared emulsion at a given temperature in an oven.
421 At regular intervals, a sample was taken and the droplet size distribution measured. For each distribution, the mean diameter
422 D was determined from the first moment of the size distribution function $D[1;0] = \frac{\sum n_i D_i}{\sum n_i}$. For each temperature, the
423 experiment was performed twice.

425 Methods 5: ^1H NMR relaxometry

426 ^1H NMR (Nuclear Magnetic Resonance) spectroscopy was performed on a 600 MHz Bruker Avance III HD spectrometer
427 (Bruker Biospin) at Martinos Center for Biomedical Imaging, Massachusetts General Hospital. T_2 relaxation was measured
428 by CPMG (Carr-Purcell-Meiboom-Gill) pulse sequence with an echo time of 1 ms. Integration over 1 kHz around the
429 PDMS signal was performed to obtain the PDMS signals for all echo decay times from 1 to 200 ms. The signal was further
430 processed by the Fast Laplace Inversion algorithm to obtain the T_2 distributions (28).

432 Methods 6: ϕ_{int} measurement

433 Emulsion samples were prepared following the procedure described in Method 1. At ϕ^* , when phase inversion occurred,
434 10 – 50 μL of a 20% PVA solution was added to the inverted emulsion in order to stabilize the globules and enable further
435 processing. Around 400 μL of emulsion was then introduced into a polyamide centrifugation tube (LUM GmbH, 2 mm
436 thick). The emulsion was centrifuged (LumiFuge™) for 30 min at 2300 g (4000 RPM). This step allowed all globules to
437 coalesce under compression without altering the stability of the internal emulsion. After centrifugation, the sample turned
438 into a cream layer containing the internal W/O emulsion on top of the extracted external water phase. Measurement of the
439 cream layer volume fraction ϕ_{cream} thanks to the optical analysis provided by the SEPView software helped deducing ϕ_{int} ,
440 as $\phi_{\text{int}} = 1 - \frac{1-\phi^*}{\phi_{\text{cream}}}$. Each emulsion was prepared three times for reproducibility testing.

442 **Supplementary Text**

444 PDMS oil purification protocol

445 Concentrated water-in-PDMS oil emulsions have been previously described in the literature (29, 30). Although these
446 emulsions were also containing cross linkers they were not supposed to contain surfactant. Some authors did attribute the
447 surprising persistence of these emulsions before being polymerized to a preferential adsorption of short-chain PDMS
448 molecules acting as surfactants. In order to investigate the role of these molecules, we performed a fractionation protocol
449 of PDMS oil (31). 20 mL of PDMS oil was vigorously mixed with 60 mL of acetone in a separating funnel. After complete
450 phase separation, the PDMS fraction was recovered and placed first in an oven at 65°C for 24h and under vacuum for
451 another 24h for complete removal of residual acetone. Fractionated PDMS oil was then used for emulsification. No
452 significant difference was noticed compared to a non-fractionated sample.

453 Comparison to other measurements of the adhesive energy

454 The value measured for the adhesive energy, ε , for the surfactant free glycerol-in-PDMS emulsion can be compared to that
455 measured with the same experimental method for a surfactant-stabilized inverse emulsion, consisting of water drops in
456 dodecane, stabilized by sorbitan monooleate (SPAN 80). By adding 25% by volume silicone oil to dodecane, the solubility
457 of the SPAN 80 is reduced, inducing an attractive interaction between the water droplets. When the concentration of the
458 poor solvent, silicone oil, is below the threshold concentration for surfactant precipitation in the dodecane-silicone-oil
459 mixture, the attractive interaction is weak and is measured to be $\varepsilon = 2 \times 10^{-2} \text{ mJ/m}^2$ (8). This value is nearly identical to
460 that measured here for the glycerol-in-PDMS emulsion, where we find $\varepsilon = 3 \times 10^{-2} \text{ mJ/m}^2$. Interestingly, in both cases,
461 the adhesive energy originates from similar mechanisms. In the case of the surfactant free emulsion, it is an intrinsic
462 consequence of the oil adsorption, whereas in the case of the surfactant stabilized emulsion, it is a consequence of the quality
463 of the solvent that is modified by adding a fourth component. This adhesive interaction induces similar consequences in
464 both systems: the gelation of the droplet dispersion into large and dense clusters that can percolate across the whole sample.

465 Capillary model for nucleation and growth

In the paper, we consider a thin film of constant thickness, and use the capillary model to determine the nucleation and growth of a hole that leads to coalescence of the droplets. The thickness of the thin film is set by the wetting of the interfaces. According to the capillary model, the energy related to the nucleation and growth of a hole of radius r within a liquid film writes $E(r) = -2\pi r^2\gamma + 2\pi r\Gamma$, where γ is the surface tension and Γ is the line tension. The first term of this equation accounts for the decrease of surface area within the film while the second term accounts for all contributions associated with the inherent high curvature at the edge of the hole. Considering these two opposite contributions, there must exist a critical radius r^* for which the growth of the pore is energetically favored. For $r = r^*$, the value of the resulting energy is expressed as an activation energy E_a . By taking the derivative, one can get $\frac{dE(r)}{dr}|_{r^*} = -4\pi r^*\gamma + 2\pi\Gamma = 0$. An expression of r^* can thus be directly deduced $r^* = \frac{\Gamma}{2\gamma}$. Finally, the expression of E_a which equals $E(r^*)$ can only be written as a function of r^* and γ . This leads to $r^* = \left(\frac{E_a}{2\pi\gamma}\right)^{1/2}$. This capillary model is appropriate for the conditions of a metastable interface of constant thickness, as is the case in these experiments.

Thin film instability

An alternative approach to treat the instability of a thin film is to consider the effect of thermally induced capillary waves on each interface in the presence of an attractive interaction due to van der Waals forces, and to calculate the time it takes for the interfaces to touch leading to coalescence.

We evaluate an effective viscosity of PDMS in the adhesive patch by using the timescale of the film rupture, initially at rest, due to the amplification of thermal thickness fluctuations by van der Waals attraction (32). The free energy cost due to interfacial tension imposes a critical wavelength λ_c of such fluctuations below which they are not amplified (33)

$$\lambda_c = \left(\frac{-2\pi^2\gamma}{\left(\frac{d^2E}{dh^2}\right)_0} \right)^{1/2} \quad (1)$$

where γ is the interfacial tension and $E(h)$ is the free energy of interaction per unit surface which is a function of the film thickness h . When repulsive forces are small compared to attractive ones, one can consider only van der Waals attraction,

$$E(h) = -\frac{A}{12\pi h^2} \quad (2)$$

where A is the Hamaker constant which can be approximated by

$$A = \frac{3}{4}kT \left(\frac{\epsilon_d - \epsilon_c}{\epsilon_d + \epsilon_c} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_d^2 - n_c^2)^2}{(n_d^2 + n_c^2)^{3/2}} \quad (3)$$

with ϵ_d , ϵ_c , n_d and n_c being the static dielectric constant and the refractive index in the visible of the dispersed phase and the continuous phase, respectively, and ν_e is the main electronic absorption frequency in the UV (34). For the system

493 composed of glycerol and PDMS oil, the theoretical estimation of A is equal to 3.8×10^{-21} J. The critical wavelength is
 494 then

$$496 \quad \lambda_c = h_0^2 \left(\frac{4\pi^3\gamma}{A} \right)^{1/2} \quad (4)$$

495
 497 where h_0 is the average film thickness.

498 The growth kinetics of the thickness modulations depends on viscous resistance of the liquid flow which is mainly related
 499 to the viscosity η of the liquid in the film. A perturbation with a wavelength λ close to λ_c has a low growth rate σ since the
 500 restoring force due to the interfacial tension is high. The capillary pressure is proportional to the curvature which varies as
 501 $1/\lambda^2$ and acts against the flow from the node to the crest of the thickness modulations (**fig. S2**). A perturbation with a long
 502 wavelength also has a low growth rate because fluid has to move over a long distance. Therefore, there exists a wavelength
 503 λ_m leading to a maximum growth rate $\sigma_m = 1/\tau_m$ which can be deduced by a linear stability analysis (35) leading to

$$504 \quad \lambda_m = \sqrt{2}\lambda_c \quad (5)$$

505 and

$$506 \quad \tau_m = \frac{96\pi^2\gamma\eta h_0^5}{A^2} \quad (6)$$

507 A small perturbation δh of the thickness will then grow exponentially with time with a characteristic time τ_m , i.e. $h = h_0 +$
 508 $\delta h e^{t/\tau_m} \sin 2\pi x/\lambda$ with x being a coordinate parallel to the average film interface (**fig. S2**).

509 The average time of film breakup t_b can be estimated by assuming that rupture occurs when the mean square of the thickness
 510 deviation from the average thickness, i.e. $\overline{h^2 - h_0^2}$ is of the order of h_0^2 . By solely considering the most amplified mode and
 511 using the principle of equipartition, the following equation is obtained (33)

$$512 \quad h_0^2 \approx \frac{kT}{2\gamma\pi^{1/2}} \frac{e^{2t_b/\tau_m}}{(2t_b/\tau_m)^{1/2}} \quad (7)$$

513 The solution of eq. (7) then gives a linear relationship between t_b and τ_m , $t_b = f(h_0, \gamma)\tau_m$. Using eq. (6), the viscosity of
 514 the liquid in the liquid film is

$$515 \quad \eta = \frac{A^2 t_b}{96\pi^2 \gamma h_0^5 f} \quad (8)$$

516 We assume here that adhesion leads to the formation of a thin film that is twice the distance from the PDMS-water interface
 517 where the order parameter of methyl group of PMDS determined by molecular dynamics simulations is higher than the
 518 average one of the bulk phase (20), which is about 1 nm. An estimate for the adhesive film thickness h_0 is thus 2 nm. If we

519 assume that t_b corresponds to the characteristic time of let size evolution $1/\omega$ (**Fig. 2**), which is about 4.3 h at 25°C, we
520 can estimate a corresponding viscosity of the order of 10^5 Pa.s where f evaluated from eq. (7) is about 2.6.

521 Rationalizing the observed long lifetime of glycerol in PDMS emulsions by using thin film instability mechanism also
522 requires a large increase of the oil viscosity in the adhesive patch as compared to its bulk value. However, this model does
523 not take into account the wetting of the interfaces which leads to an equilibrium thickness set by a short range repulsion,
524 and intrinsically results in the existence of an activation energy. For this reason, the nucleation model is a better description
525 of the behavior.

526 Other contributions to the adhesion observed in emulsions: double layer effects and van der Waals interactions

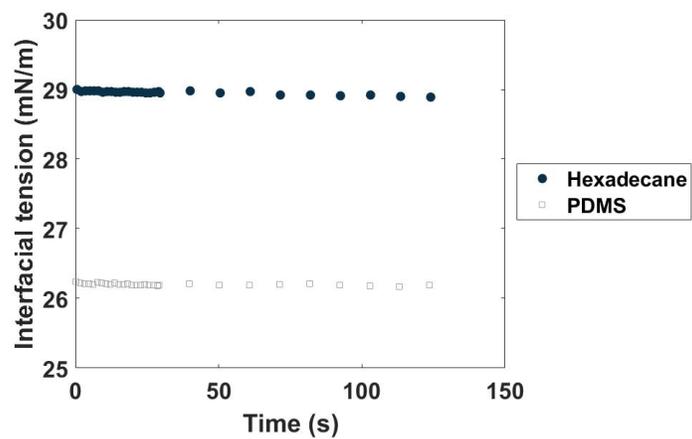
527 Since there is no charge in the system, there are no double layer effects. In order to confirm this, we have added salt into
528 the dispersed phase up to 0.5 mol/L and verify that the entire phenomenology was conserved. By contrast van der Waals
529 interactions should be present and could also contribute to the overall adhesion that we observe. However, when we use
530 different molecular weight oils of the same nature (PDMS oil for example) for which the magnitude of van der Waals
531 interactions should be the same, we observe a gradual decrease of the adhesion when the molecular weight decreases, until
532 it disappears at which point the droplets are no longer stable. These results suggest that van der Waals interactions are not
533 the dominant contribution in the formation of this adhesive patch although they are important in driving the growth of the
534 hole for droplets to coalesce.

535 Decay of P_1 peak intensity in the NMR relaxation experiment

536 The contribution to the P_1 peak is primarily the oil in the thin adhesive film located between neighboring droplets. At volume
537 fraction of 60% the droplets are at roughly random close packing in which case the average number of nearest neighbors is
538 6. By contrast at volume fraction of 76% the packing is much denser and roughly hexagonal which increases the average
539 number of nearest neighbors to about 10, which is increased even further by polydispersity. Accordingly, the number of
540 PDMS molecules probed through the NMR relaxometry strongly rises. Hence the change in the peak amplitude from 76%
541 to 60% volume fraction.

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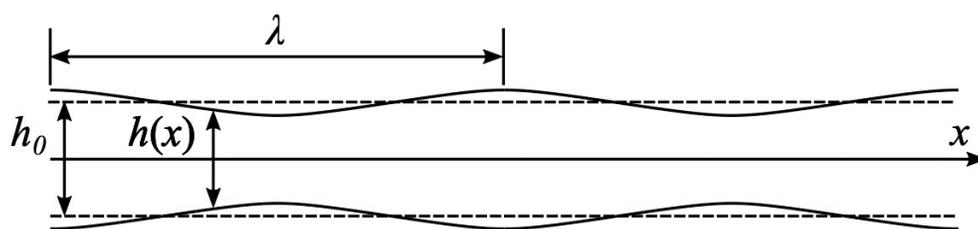
545 **fig. S1. Interfacial tension evolution over time of a glycerol droplet in oil.** PDMS oil was fractionated prior to this
546 measurement. The interfacial tension (IFT) remains stable over time, confirming the purity of the oil.

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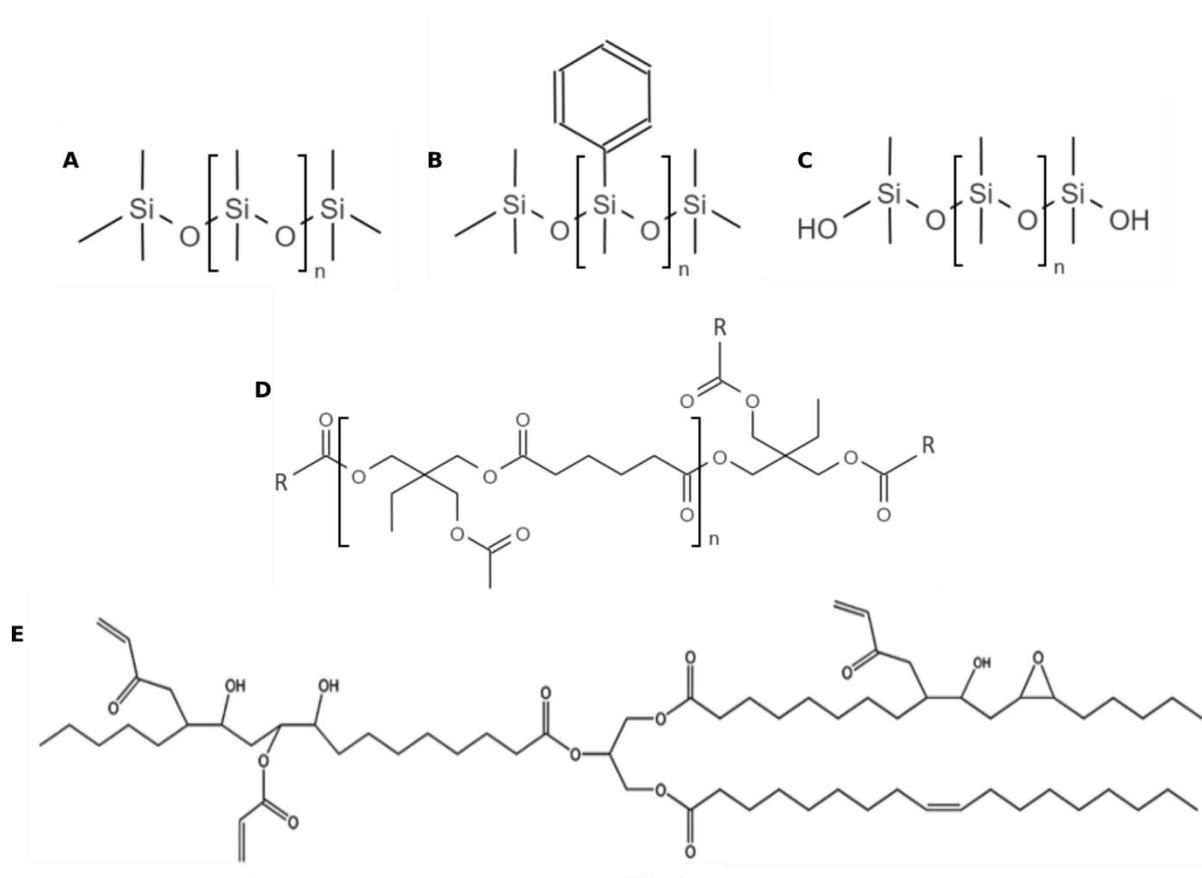
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551

552 **fig. S2. Sinusoidal modulation with a wavelength λ of the thickness of a thin liquid film.** The film has an average
553 thickness h_0 .
554



556

557

558

fig. S3. Examples of oil polymeric backbones. (A), PDMS methyl terminated. (B), PPMS. (C), PDMS hydroxy terminated. (D), Polyester. (E), Acrylated soybean oil

559

560 **Movie S1. Coalescence event in a glycerol-in-PDMS emulsion.** A glycerol-in-PDMS emulsion is obtained by dispersing
561 about 1% by volume of glycerol into PDMS oil ($\eta = 350$ cp). We deposit 20 μL of this emulsion on a glass slide and
562 directly observe with a microscope (X10) at $T = 60^\circ\text{C}$. The emulsion evolution is recorded for a duration of 200 s with a
563 frame captured every 2 s. The number of doublets within the recorded zone is evaluated to be around 100. During the entire
564 recording period the number of coalescence events which are observed within this zone is about 5, which suggests a
565 coalescence frequency per doublet of about $2.5 \cdot 10^{-4} \text{s}^{-1}$. This is in agreement with the value of $\omega = 5 \cdot 10^{-4} \text{s}^{-1}$ deduced
566 from the coarsening of a dense emulsion at 60°C . In this movie, we focus on just one of these events which occurs between
567 the frames at 32 and 34 s: Two adhesive droplets of about 10 microns in diameter within a linear triplet suddenly merge as
568 a result of coalescence. The scale bar is 10 μm .

569

570