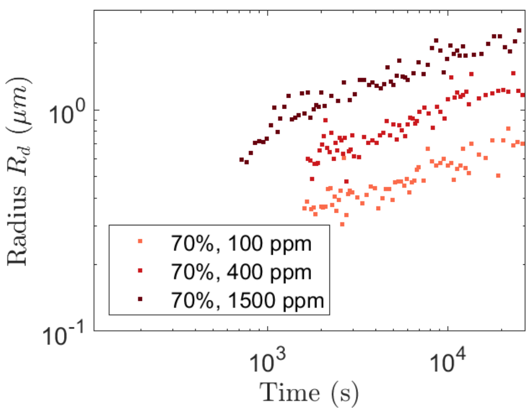
Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information, Delance et al.

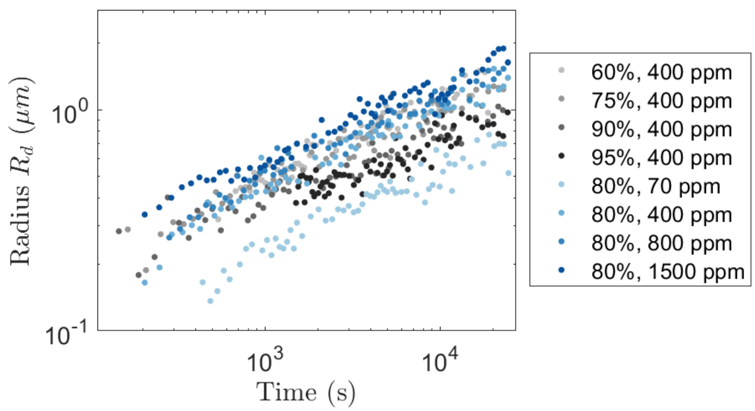
June 3, 2024

1 Emulsion microdroplet radius evolution over time

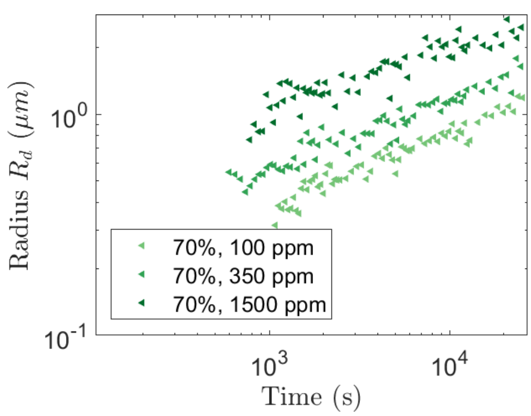
Within the emulsion, emulsified microdroplets coalesce through a diffusion limited process [?]. The microdroplet radius has been measured over time using Dynamic Light Scattering for the three PDMS grades. Results are shown in Fig.1.



(a) 5 000 $mm^2 s^{-1}$



(b) 60 000 $mm^2 s^{-1}$



(c) 300 000 $mm^2 s^{-1}$

Figure 1 Droplet radius evolution over time for the three PDMS grades. Legend: mass fraction in cyclopentanol (%) and mass fraction in PDMS (ppm). 1 ppm$= 10^{-6}$ kg/kg.

In a previous work (Delance *et al.*, Soft Matter, 2022) we rationalized the mechanism by which the microdroplets diffuse by brownian motion in the continuous phase until they coalesce so that the evolution of their mean radius R_d follows the equation:

$$R_d \simeq R_0 \left(\frac{t}{\tau_c}\right)^{1/3}. \tag{1}$$

with

$$\tau_c = \frac{2\pi\eta_c R_0^3}{k_B T \phi}, \tag{2}$$

where R_0 is the radius of the droplets at time $t = 0$ of mixing the three liquids, η_c the viscosity of the continuous liquid phase, $k_B T$ the thermal energy, and ϕ is the droplet volume fraction. In Fig.2, we plot the measured radius against the radius that we can calculate using these equations. We find that all data collapse on a master curve, which confirms our hypothesis that the radius of the microdroplets increases due to coalescence. This result holds for the three different PDMS grades.

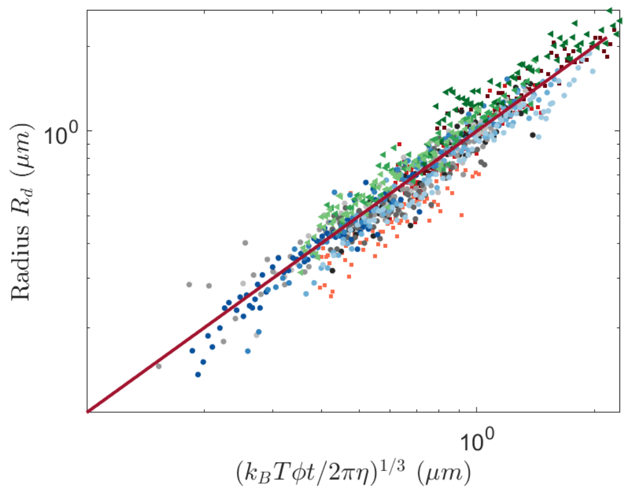


Figure 2 Measured radius as a function of the theoretical radius computed using Eq. 1 and 2 for the three PDMS grades.

2 Dispersed phase composition and viscosity as a function of the PDMS grade

In this section, we measure the composition and viscosity of the dispersed phase. We first separate the dispersed phase from the continuous one. To do so, we wait for the microdroplets to sediment at the bottom of the vial and we then simply extracted this phase with a syringe. We then measure the composition by infrared spectroscopy
In Table 1, we present the composition of the dispersed phase as a function of PDMS grade. The uncertainty on the measurements is $\pm 2\%$. The composition slightly varies depending on the PDMS grade by less than 6%. Thus, we consider that the changes in the composition of the dispersed phase depending on the PDMS grade do not affect the thin film experiments.

PDMS viscosity	5000 $mm^2\,s^{-1}$	60000 $mm^2\,s^{-1}$	300000 $mm^2\,s^{-1}$
PDMS (%)	60	66	59
Cyclopentanol (%)	17	11	17
Decane (%)	23	23	24

Table 1 Droplet composition for different PDMS viscosities. (mass fraction in %)

The viscosity of the dispersed phase was then measured using a rheometer (TA DHR3, cone-plane geometry). We note that due to the composition and the presence of decane and cyclopentanol, the droplet viscosity is lower than the initial PDMS viscosity. The results for the three PDMS grades are presented in Table 2.

Molar mass ($g\,mol^{-1}$)	49350	116000	204000
Kinematic viscosity of PDMS ($mm^2\,s^{-1}$)	5000	60000	300000
Dynamic viscosity of PDMS (Pa s)	4.87	59	294
Dynamic viscosity of the droplets (Pa s)	0.3	6	27

Table 2 Newtonian viscosity of the droplets depending on the PDMS grade

Note that for the largest grades, shear thinning is measured starting from a shear rate of 500 s^{-1} and 1 s^{-1} respectively. The viscosity of the continuous phase η_c was also measured with a rheometer (Low Shear 400, Lamy rheology). We found $\eta_c = 3.5 \cdot 10^{-3}$ Pa.s.

3 Histograms of lifetimes versus observed mechanisms

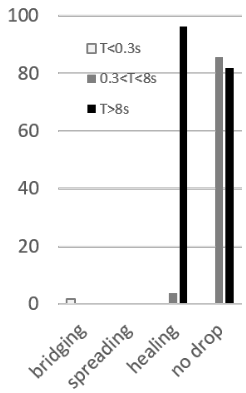
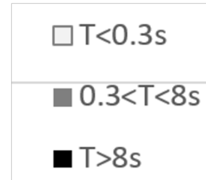
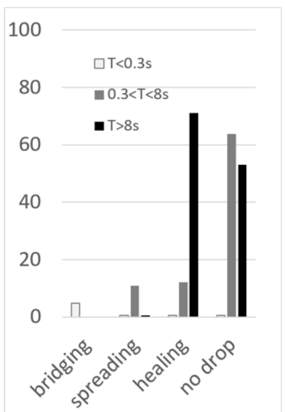
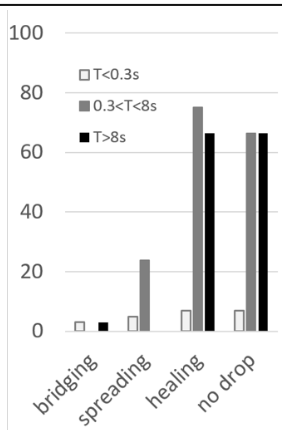
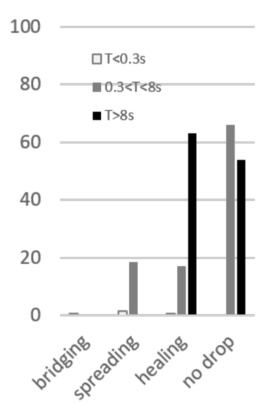
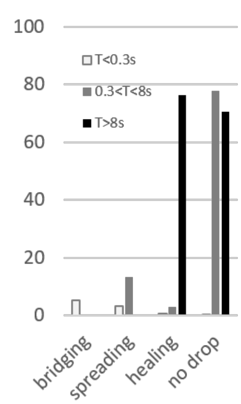
<table>
<tr><td></td><td>R_d=1.2 µm</td><td>1 µm</td><td>0.7 µm</td></tr>
<tr><td>η_d=
0.3 Pa.s</td><td></td><td></td><td></td></tr>
<tr><td>6 Pa.s</td><td></td><td></td><td></td></tr>
<tr><td>27 Pa.s</td><td></td><td></td><td></td></tr>
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Figure 3 Histograms of lifetimes as a function of the observed mechanism for different emulsion droplet size R_d and dispersed phase Newtonian shear viscosity η_d. "spreading" corresponds to cases where a local thinning is observed that leads to bursting. The occurrence of 'spreading' increases with the dispersed phase viscosity and the droplet radius. 'healing' and 'no drop' are predominant when the microdroplets are inefficient at inducing film bursting (low viscosity and low droplet size). 'bridging' is rare in all cases and corresponds to the shortest lifetimes.