Supporting Information

Complex High Internal-Phase Emulsions that can Form Interfacial Films with Tunable Morphologies

Tao Li,[*,†,‡,§] Ruipei Xie,[§] Wei Chen,[†,‡] Andrew B. Schofield,[‖] and Paul S. Clegg[‖]

[†] Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou, Zhejiang 325001, P. R. China.

[‡] Oujiang Laboratory (Zhejiang Lab for Regenerative Medicine, Vision and Brain Health), Wenzhou, Zhejiang 325001, China.

[§] Beijing National Laboratory for Condensed Matter Physics and Key Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[‖] School of Physics and Astronomy, University of Edinburgh, James Clerk Maxwell Building, Peter Guthrie Tait Road, Edinburgh, EH9 3FD, UK.

KEYWORDS: High internal phase emulsion, Interfacial films, Soft matter, Janus HIPE, Droplets

Corresponding Author: litao@ucas.ac.cn (Dr. Tao Li)

Table of contents:

Figure S1. Two-dimensional fast Fourier transform (2D-FFT) patterns of castor oil droplets. Generally, when the droplets were aligned in one direction, the spatial frequency parallel with the direction is low and the spatial frequency perpendicular to the direction is high. The spatial frequency in pattern (a) exhibits a slightly higher intensity in both horizontal and vertical directions, reflecting a random distribution of the droplets. Pattern (b) has a higher intensity of the spatial frequency in horizontal direction, suggesting that the droplets arrays are relative ordering in the vertical direction. Pattern (c) indicates that the droplets are more ordering in both directions.

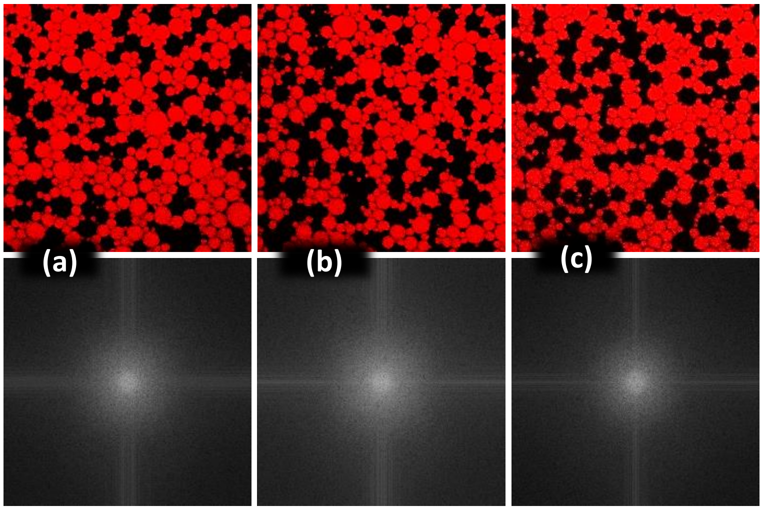


Figure S2. The micro-structures of “single” HIPEs and double HIPEs (the scale bar =50 µm). All systems are created by shearing at 8K rpm for 40s; the water phase contains SDS and silica nanoparticles.

(a) A HIPE system formed just by castor oil (~600 cSt). Droplet diameter = 5.4±0.4 µm; average distance between droplets ~ 1.1 µm.

(b) A “single” HIPE formed just by silicone oil (10 cSt). Droplet diameter = 21.6±0.8 µm; average distance between droplets ~ 3.8 µm. (c) A double HIPE formed by silicone oil (10 cSt) and castor oil. Droplet diameter = 6.5±0.8 µm; average distance between droplets ~ 1.3 µm.

(d) A “single” HIPE formed just by silicone oil (50 cSt). Droplet diameter = 22.1±0.7 µm; average distance between droplets ~ 3.1 µm. (e) A double HIPE formed by silicone oil (50 cSt) and castor oil. Droplet diameter =6.4±0.8 µm; average distance between droplets ~ 1.2 µm.

(f) A “single” HIPE formed just by silicone oil (1000 cSt). Droplet diameter = 17.6±0.7 µm; average distance between droplets ~ 3.4 µm. (g) A double HIPE formed by silicone oil (1000 cSt) and castor oil. Droplet diameter =6.7±1.1 µm; average distance between droplets ~ 0.9 µm.

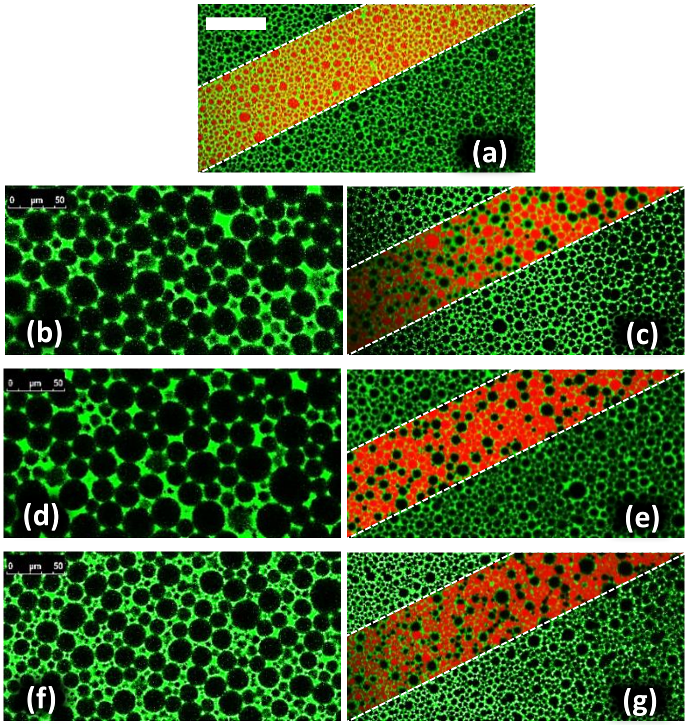


Figure S3. (a) The emulsion created by shearing 1.5g of silicone oil, 1.5g of isopropyl myristate and 0.5g of aqueous solution (water with 4mg of SDS and 6mg of silica nanoparticles) at 8000 rpm (~13700 s^{-1}) for 40 seconds. Since silicone oil and isopropyl myristate are miscible, the system exhibits conventional oil-in-water emulsions. (b) Using castor oil and mineral oil can creates a HIPE system with complex micro-morphologies, including single-oil droplets, core-shell droplets, and Janus structures with different contact angles. Moreover, the droplet size is of very uneven distribution. Scale bar= 50 µm.

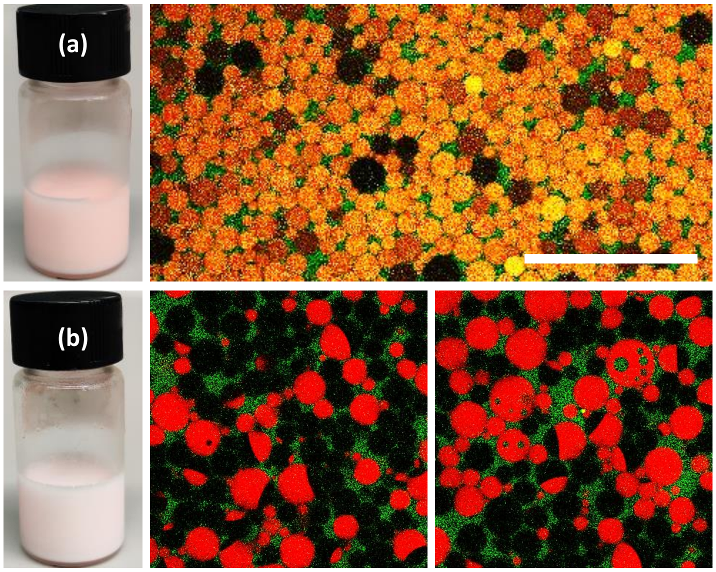


Figure S4. The micro-structure of a double HIPE system formed without silica particles. Scale bar= 50 µm.

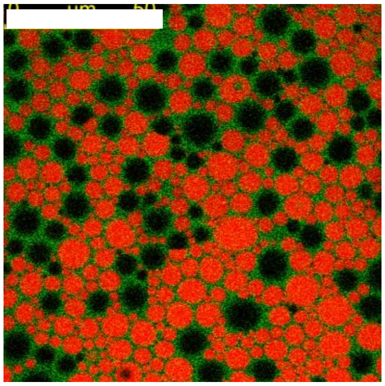


Figure S5. The measured elastic modulus (G’) and loss modulus (G’’) for double HIPEs with nanoparticles (dark blue) and without nanoparticles (light blue). Both systems contain an aqueous phase (water and SDS), silicone oil (~50 cSt) and castor oil, and were sheared at the same rate (8K rpm) for 40s.

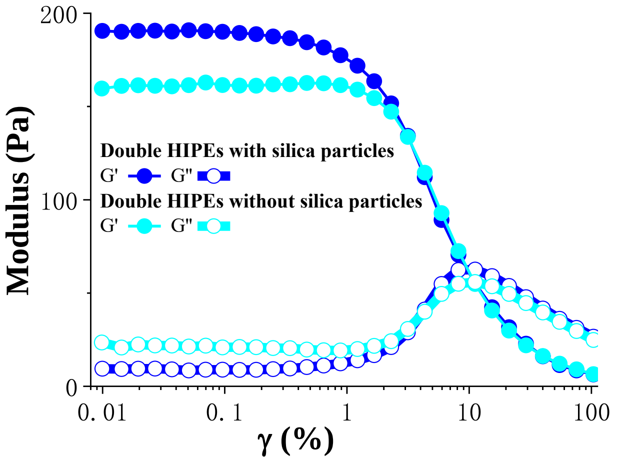


Figure S6. Thixotropic profile of the double HIPE measured versus shear rate at room temperature.

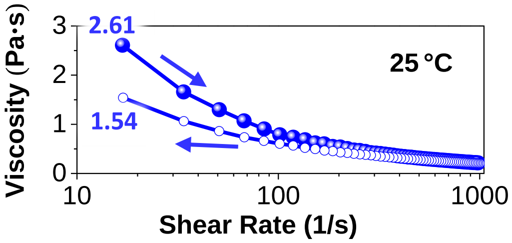


Table S1. The measured interfacial tensions between water, silicone oil and castor oil with the added fluorescent dyes and surfactants. All the values are obtained statically at room temperature. SDS adsorbs at the oil–water interface rapidly, which therefore significantly reduces the interfacial tensions between water and the oil.

Liquid & liquid	**Measured interfacial tension**
Silicone oil (50 mPa·s) & Water	~ 37.2 mN/m
Silicone oil (50 mPa·s) & water (with SDS) / Water (with SDS and Ethanol)	~12.0 mN/m /~13.3 mN/m
Castor oil (with Nile red) & Water	~ 23.1 mN/m
Castor oil (with Nile red) & Water (with SDS) / Water (with SDS and Ethanol)	~ 2.2 mN/m /~5.8 mN/m
Silicone oil (50 mPa·s) & Castor oil (with Nile red)	~ 3.2 mN/m

Table S2. The measured interfacial tensions between water, silicone oil and sunflower oil with the added fluorescent dyes and surfactants. All the values are obtained statically at room temperature.

Liquid & liquid	**Measured interfacial tension**
Silicone oil (50 mPa·s) & Water	~ 37.2 mN/m
Silicone oil (50 mPa·s) & Water (with SDS)	~12.0 mN/m
Sunflower oil (with Nile red) & Water	~ 23.1 mN/m
Sunflower oil (with Nile red) & Water (with SDS)	~3.2 mN/m
Silicone oil (50 mPa·s) & Sunflower oil (with Nile red)	~ 2.1 mN/m

Discussion on Princen and Kiss model

In 1986, Princen and Kiss (see Ref.1) presented the following expression for static shear modulus of a series of concentrated oil-in-water emulsions, which is now widely used as an empirical model for the elastic modulus of a HIPE system:

$$G' = 1.769\ \Phi^{\frac{1}{3}}(\Phi - 0.712)\frac{\sigma}{d} \tag{S1}$$

where Φ (> 0.712) represents the equivalent volume fraction of the dispersed phase (note Φ is not only the dispersed phase volume fraction, but also relates to the film thickness between the droplets), σ is the interfacial tension, and d is the mean radius of the droplets. The synergistic effect created between silicone oil and castor oil is first embodied in d. As shown in Figure 1g, d of the castor oil-HIPE is 2.7 ± 0.2 µm, with an average distance ~ 1.1 µm between each other. All HIPEs formed by different viscous silicone oils have a 3-4 times larger d, and a larger distance (> 3µm) between the droplets (Figure 1h and Figure S2). Mixing these two liquids, obviously, decreases the size of the silicone oil droplets remarkably, making them comparable to the castor oil droplets (Figure 1i and Figure S2). Meanwhile, for the double HIPEs, the parameter σ (which can be written as σ_{double}) is also quite complex, since it contains both $\sigma_{castor\ oil\ \&\ water}$ (~2.2 mN/m, see Table S1 below) and $\sigma_{silicone\ oil\ \&\ water}$ (~12.0 mN/m, Table S1). The value of σ_{double}, however, is not necessary in between. If we apply the upper and lower bounds for the elastic properties of nanoparticle composites,[2] which is the model of springs connected in parallel or series, σ_{double} can be smaller than $\sigma_{castor\ oil\ \&\ water}$, or larger than $\sigma_{silicone\ oil\ \&\ water}$. Currently, there is no general rule for a mixed σ. Considering the comparable size between castor oil-HIPE and the double HIPEs, we suppose the value of σ_{double} should be somehow similar to $\sigma_{castor\ oil\ \&\ water}$. One manifestation is that, the measured G' values of both double HIPEs in Figure 1f are closer to that of the castor oil-HIPE.

Previous studies of ternary polymer blends have proved that, the viscosity ratio between two dispersed phases can strongly affect its phase morphology and rheological/mechanical properties, although the related mechanisms are still not clear. In our systems, the viscosity ratio between silicone oil and castor oil may have an influence on both d and σ_{double} via the critical capillary number (Ca_{cri}), which can further affect the G' of the double HIPEs.

Discussion of the Capillary number.

The dynamics of droplets under shear is determined by the ratio between the viscous deformation stresses (shear stress) and the restoring interfacial stresses (Laplace pressure), given by the capillary number:

$$Ca = \frac{\text{shear stress}}{\text{Laplace pressure}} = \frac{\lambda\dot{\gamma}d}{\sigma} \tag{S2}$$

where $\dot{\gamma}$ is the shear rate, d is the radius of the droplets, σ is still the interfacial tension, and λ is the viscosity of the continuous phase. Once the value of Ca exceeds a critical threshold (Ca_{cri}), large droplets would deform and break up under the influence of shear. It is believed that Ca_{cri} depends on the type of flow, and the viscosity ratio between the dispersed phase and the continuous phase.[3,4] The final size of the droplets is usually a balance between coalescence and breakup of the dispersed phase:

$$d \propto\ Ca_{cri}\frac{\sigma}{\lambda\dot{\gamma}} \tag{S3}$$

It should also be noted that, the coalescence between the droplets can be very fast and stops once the interfaces of the droplets are fully coated by stabilizers. Only droplets containing the same component can coalesce, which can be helpful to limit the droplet size in the double-HIPE systems.

We should emphasize that, the parameters involved in Equation (1)-(3) may impact on each other; the effects of some other parameters, *e.g.*, the viscosity of the dispersed phase and the liquid density, still need to be confirmed.

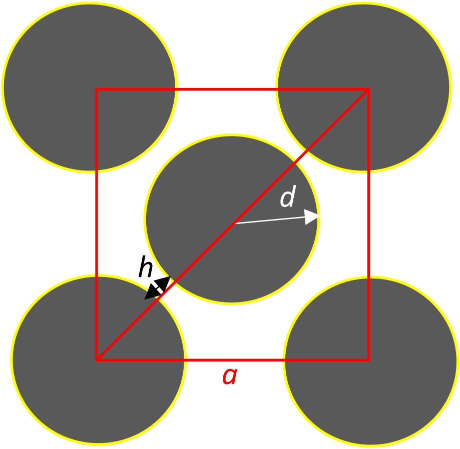
Discussion of the Internal phase concentration.

As we discussed above, Φ in Equation (1) represents the equivalent volume fraction of the dispersed phase, which relates to the finite film thickness between the droplets, *i.e.*, the distance between the droplets. Specifically,

$$\Phi^{-1/3} = \Phi_{internal}^{-1/3} - 1.105\frac{h}{2d} \tag{S4}$$

where h is the film thickness, d is the droplet radius, and $\Phi_{internal}$ is the volume fraction of the internal phase.

Equation (4) is quite complex and requires some assumptions about the relationship between h and d. If we assume that all the droplets arrange in a face-centred cubic (fcc) lattice with a distance h between each other, as illustrated below:



$$\sqrt{2}a = 4d + 2h \rightarrow a = \frac{4d+2h}{\sqrt{2}}$$

$$V_{cell} = a^3 = (\frac{4d+2h}{\sqrt{2}})^3$$

$$V_{droplets} = 4 \times \frac{4}{3}\pi d^3$$

the volume fraction of the dispersed phase $\Phi_{internal}$ is the same for all our systems. Therefore:

$$V_{droplets} = V_{cell} \times \Phi_{internal}$$

i.e.,

$$\frac{16}{3}\pi d^3 = (\frac{4d+2h}{\sqrt{2}})^3 \times \Phi_{internal} \rightarrow \frac{4\sqrt{2}}{3}\pi d^3 = (2d+h)^3 \times \Phi_{internal} \tag{S5}$$

Clearly, when d gets larger, h gets larger as well, consistent with our experimental observations (Figure S2).

Systems with small *d* and *h* have a high internal phase concentration, which can help to increase the G’ for a HIPE system as illustrated in Equation (1), and as reported in previous experiments.[5] As shown in Figure S2b, d and f), the “single” HIPEs formed just by silicone oil have relatively low internal phase concentration, which can be part of the reason for their relatively low G’.

Shearing the system with different rate can significantly change the droplet size as suggested by Equation (2). A high shearing rate can create a large number of small droplets. During coalescence, these droplets would share the continuous phase in between, get contact with each other and lose their original spherical shape (Figure 2d). This leads to a very high internal phase concentration, and can increase the G’ of the system. The opposite situation occurs when using a low shearing rate.

REFERENCES

(1) Princen, H.; Kiss, A. J. *J. Colloid Interface Sci.* **1986**, *112*, 427-437.

(2) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J. *Chem. Soc. Rev.* **2011**, *40*, 3941–3994.

(3) Mulligan, M. K.; Rothstein, J. P. *Langmuir* **2011**, *27*, 9760–9768.

(4) Welch, C. F.; Rose, G. D.; Malotky, D.; Eckersley, S. T. *Langmuir* **2006**, *22*, 1544-1550.

(5) Gutiérrez, G.; Matos, M.; Benito, J.M.; Coca, J.; Pazos, C. *Colloids Surf A.* **2014**, *442*, 111-122.