Influence of Emulsifiers on Stability and Rheological Properties of Concentrated Oil in Water Emulsions

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Outline

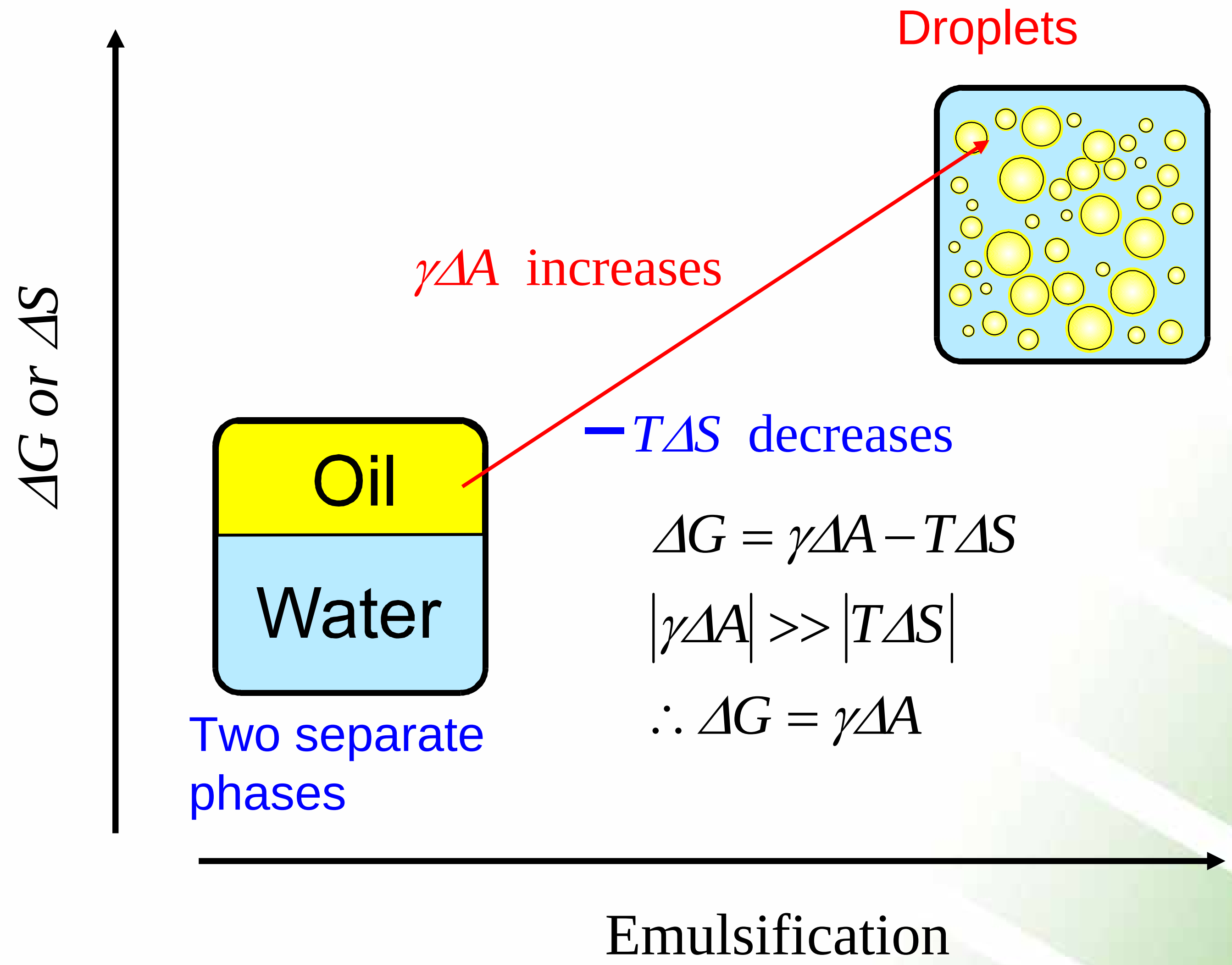
1. Introduction
2. Emulsions prepared by polymeric emulsifiers
3. Conclusions for the emulsions prepared by polymeric emulsifiers
4. Pickering emulsions
5. Conclusions for Pickering emulsions

Introduction

Emulsions, i.e. dispersions of liquid droplets stabilized by emulsifiers in a continuous liquid medium, are very interesting objects for rheological investigations. Studies of emulsions under shear flow have long been a subject of both theoretical and experimental interest and various systematic results have been reported.

Emulsions are not thermodynamically stable states and they are metastable dispersions.

Diagram of the free energy and entropy change of a system during emulsification



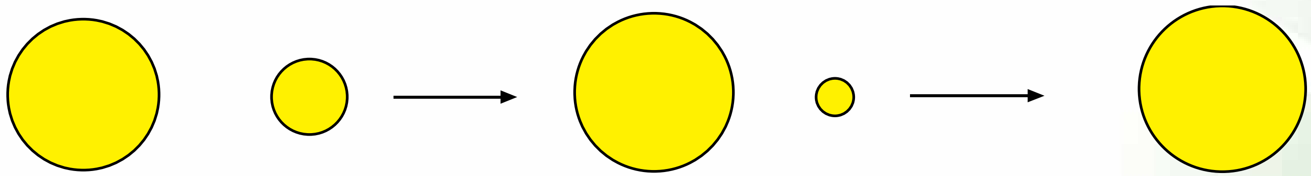
$$\Delta G = \gamma\Delta A - T\Delta S$$

$$|\gamma\Delta A| >> |T\Delta S|$$

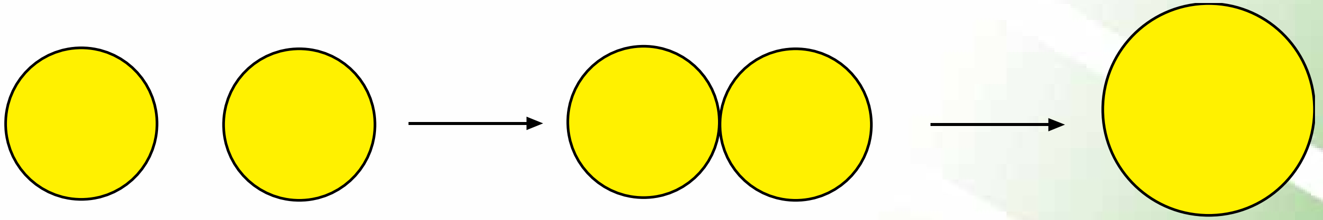
$$\therefore \Delta G = \gamma\Delta A$$

Since emulsions are metastable dispersions, instability of emulsions, such as Ostwald ripening and coalescence are not negligible.

Ostwald ripening



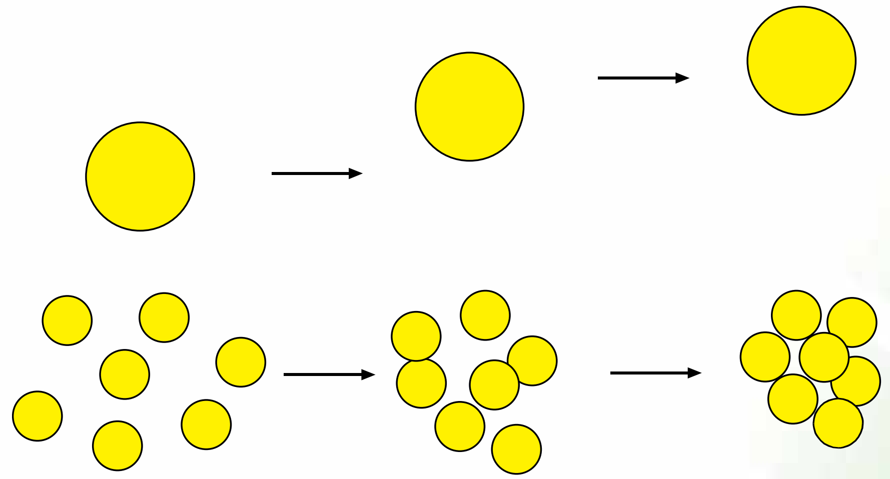
Coalescence

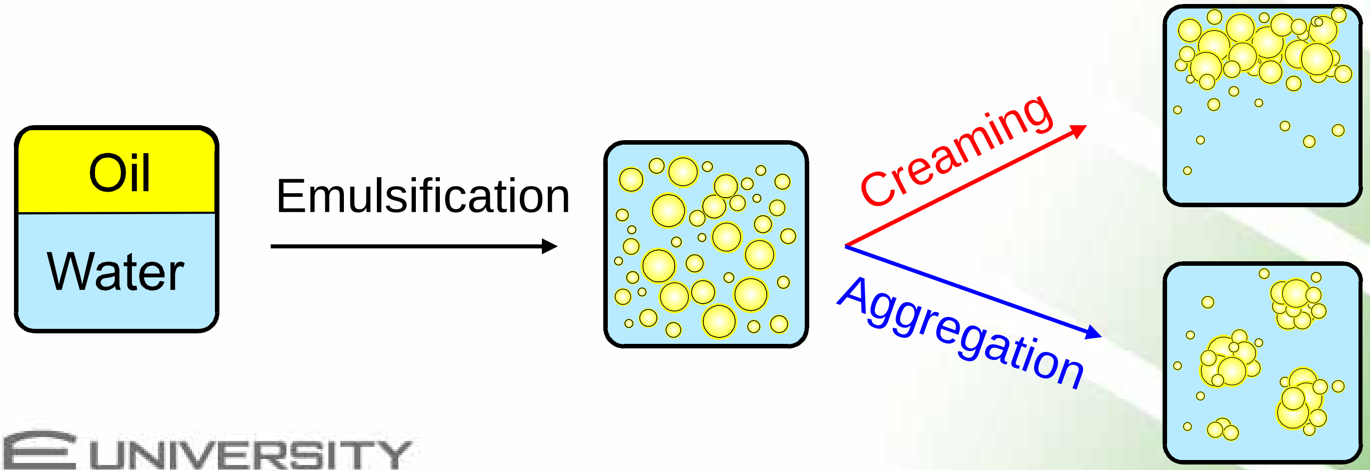


On the other hand, other instabilities such as creaming and aggregation also occur after preparation of emulsions.

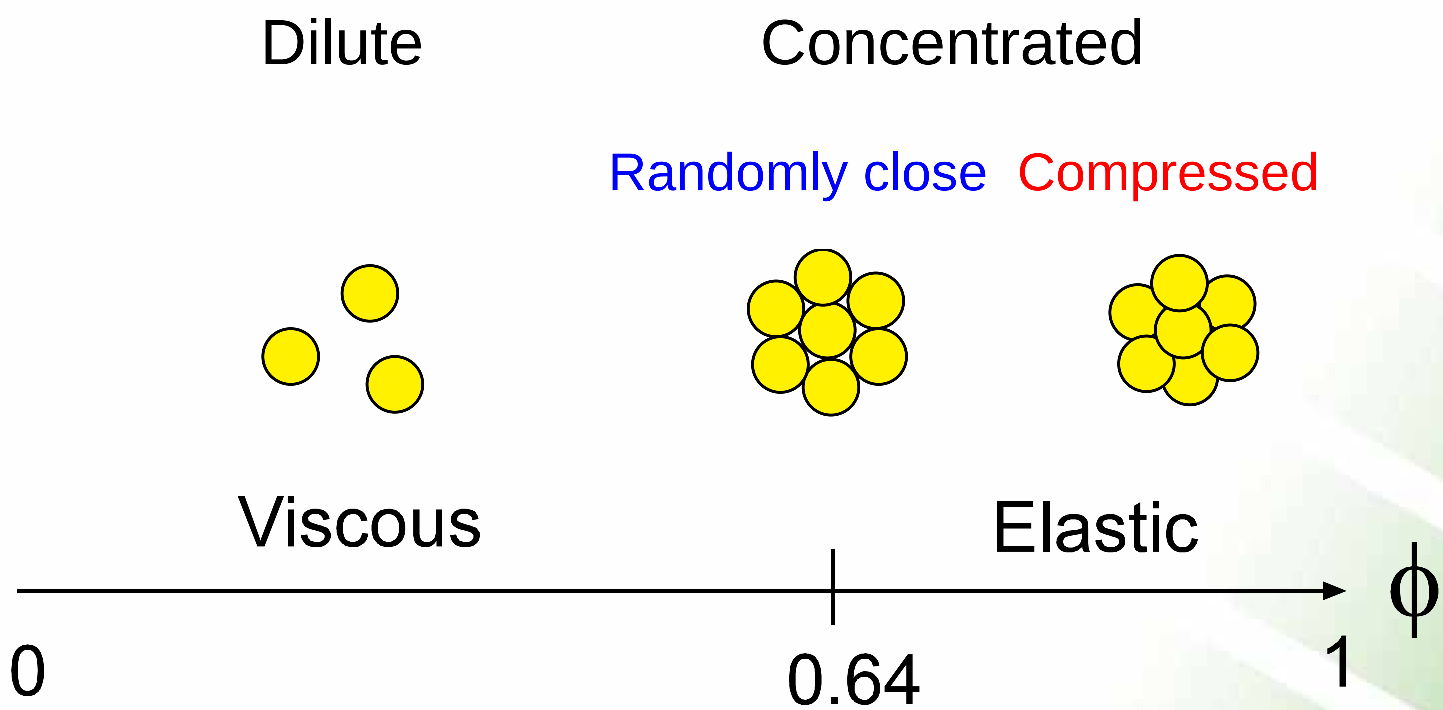
Creaming

Aggregation





Changes in rheological properties by packing of droplets



ϕ: Volume fraction of droplets in emulsified phase

$$G_{sm} = 2\frac{\sigma_{in}}{D_{3,2}}\phi(\phi - 0.64) \qquad (Mason - Bibette - Weitz)$$

Characterization of emulsions

1. Type of emulsions (Dilution method)
2. Amounts of adsorbed emulsifiers (Spectroscopic techniques)
3. Droplet Size distribution (Coulter counter, Optical microscope)
4. Stability of emulsions (Optical methods)
5. Interfacial properties
6. Emulsion rheology

In this presentation, we will force on stability and rheological properties of silicone oil droplets stabilized by some emulsifiers such as water-soluble polymers and silica particles pre-adsorbed polymers in water. The respective emulsifiers were adsorbed on the silicone oil droplets. The resulting oil in water (O/W) emulsions were classified into concentrated emulsions because their volume fraction of oil droplets in the emulsified phase was greater than 0.6. Rheological properties of the corresponding O/W emulsions have been carried out by the measurements of stress-strain curve together with the optical microscopic observation of changes in oil droplets under shear flow, and oscillatory shear viscoelasticity.

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Emulsifiers

Polymeric emulsifiers: Hydroxyl propyl methyl Cellulose (HPMC), PEO-PPO-PEO, Poly-N-isopropyl acrylamide (PNIPAM) .   Their aqueous solutions were surface active, leading to a decrease in the surface tension.

Silica particles: Hydrophilic Aerosil130 fumed silica and hydrophobic Aerosil R-972 fumed silica (silane-coupling modification of silanol groups of 130 with dimethyldichlorosilane)

Silica particles pre-adsorbed polymers: Aerosil 130 and Aerosil R-972 silica particles were pre-adsorbed by HPMC and PNIPAM below at the plateau region of adsorption isotherm of the respective polymers. The silica particles pre-adsorbed polymers were rinsed with water to remove the free polymers.

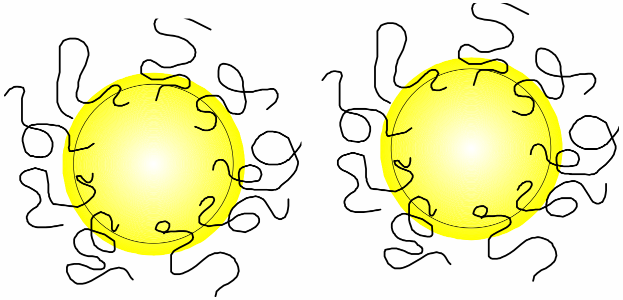
Features of emulsions stabilized by polymeric emulsifiers

Formation of an adsorbed polymer film layer thickness *h* on droplet surface provides that

1) a lager effective volume fraction $\phi_{eff} \approx \phi[1+3h/D]$, where *D* is the droplet diameter (*D*>>*h*),

2) a decrease in the deformation of the interface,

3) an increase in the repulsive forces between droplets.



Adsorbed polymeric emulsifiers in the schematic representation is extremely exaggerated.

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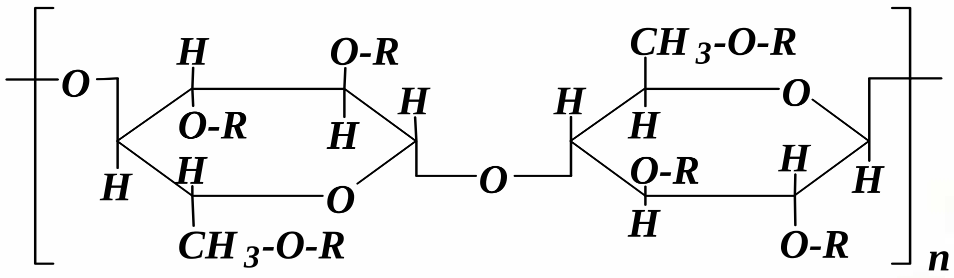
Emulsions prepared by HPMC and PEO-PPO-PEO

HPMC: 60SH-400
Mw = 380 x 10^3
C* = 0.172 g/100 mL



R : $-CH_3$, $-CH_2CH(OH)CH_3$, -H

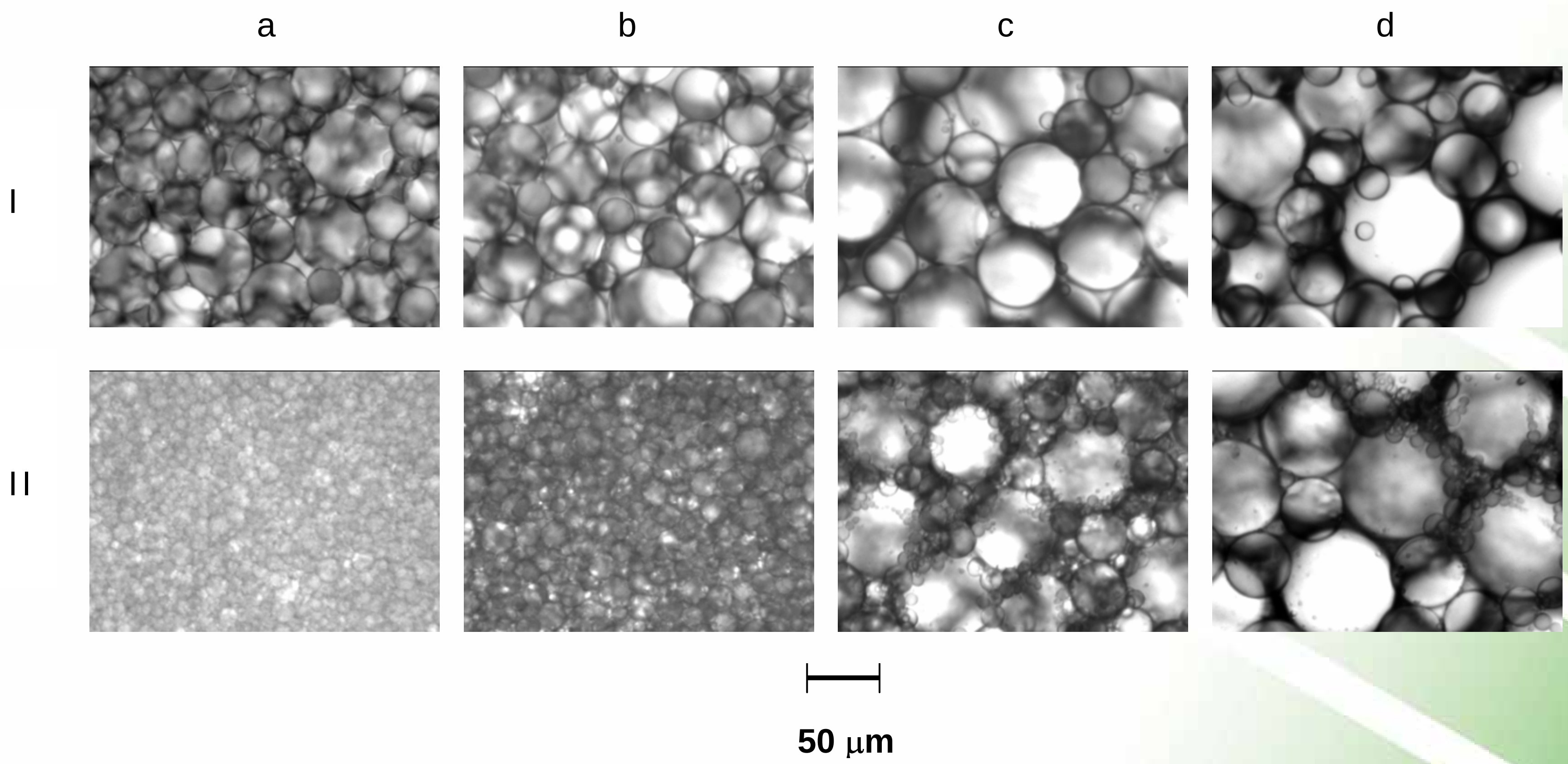
DS = 1.8 MS = 0.25

PEO-PPO-PEO: F-108, 80 wt% PEO, Mw = 15.5 x 10^3

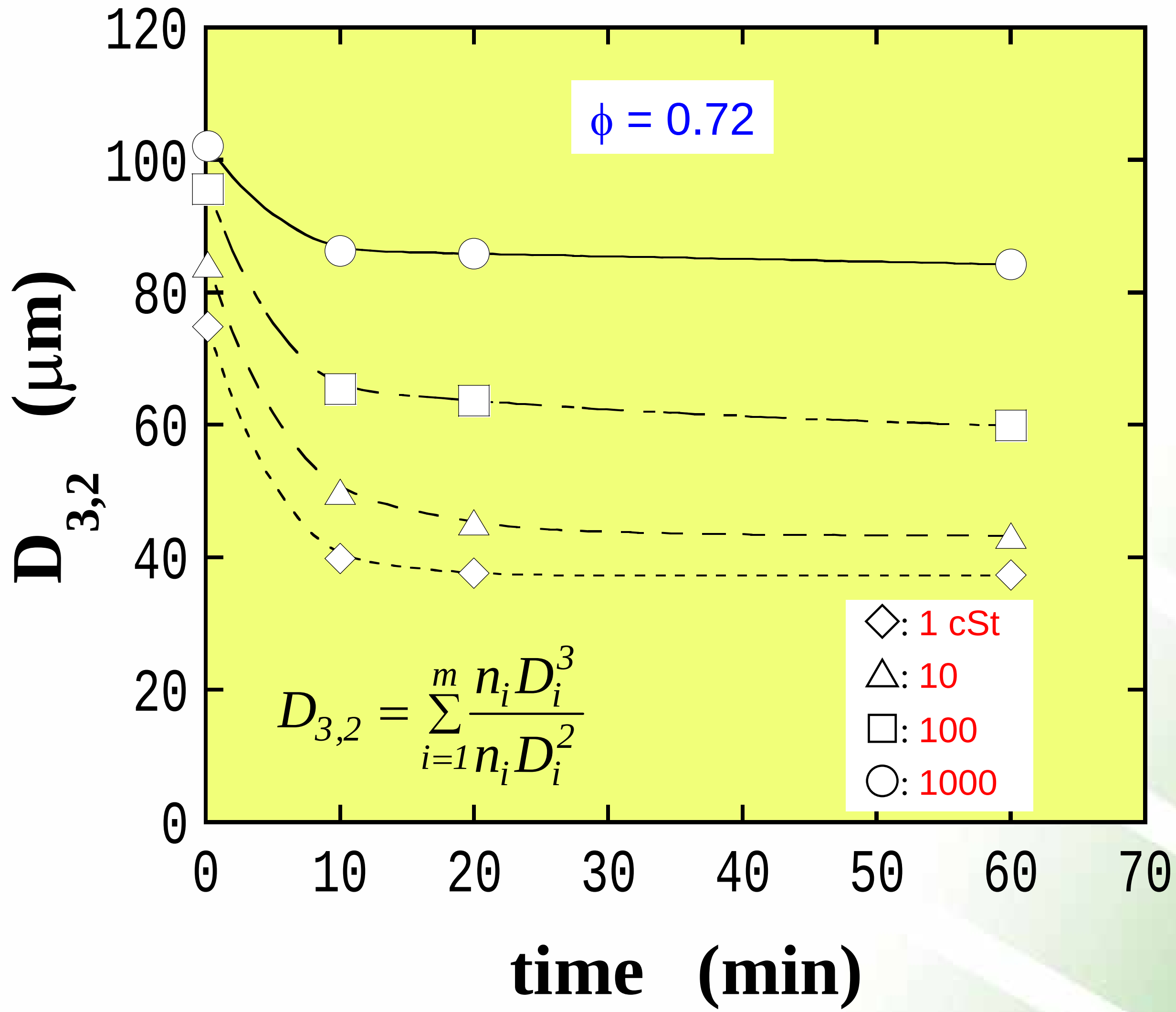
Silicone oil: KF96L-1 (1 cSt), KF96-10 (10 cSt), KF96-100 (100 cSt), KF96-1000 (1000 cSt)

Interfacial tensions of the oil/aqueous solution of HPMC and PEO-PPO-PEO are 17.3 and 8.4 mN/m, respectively.

Preparation of emulsions: 25g of silicone oil were agitated with 50g of 0.5g/100 mL aqueous solution of HPMC or PEO-PPO-PEO for given times ranging from 10 s to 60 min at 8000 rpm and 25 ^{o}C.



Optical microscopic images of silicone oil droplets prepared by HPMC (I) and PEO-PPO-PEO (II): silicone oil with kinetic viscosity of 1 (a), 10 (b), 100 (c), and 1000 cSt (d).



Plots of Sauter size $D_{3,2}$ of oil droplets of the emulsions prepared by HPMC as a function of agitation time for different silicone oils.

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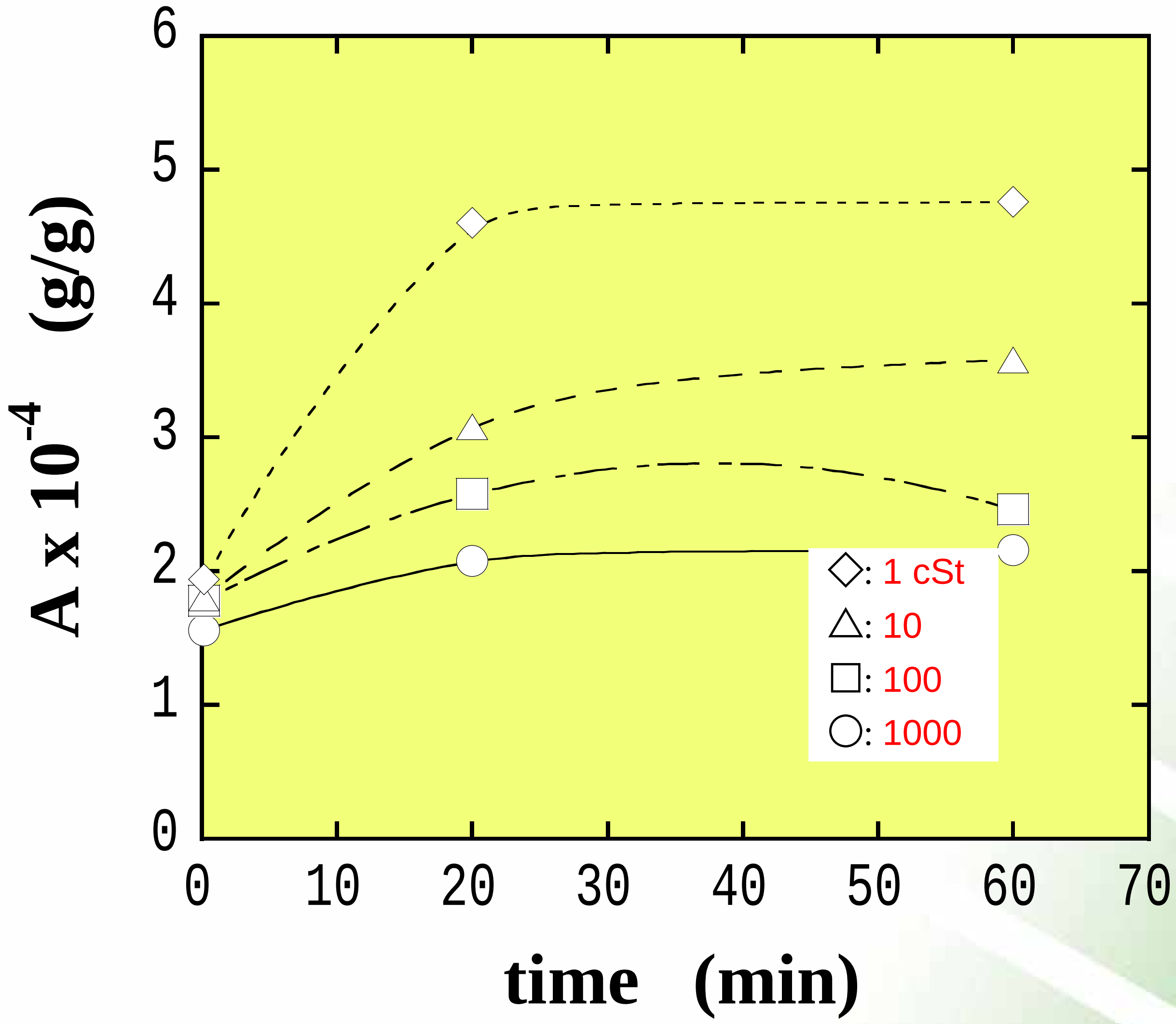

Plots of the adsorbed amounts of HPMC on oil droplets as a function of agitation time for different silicone oils.

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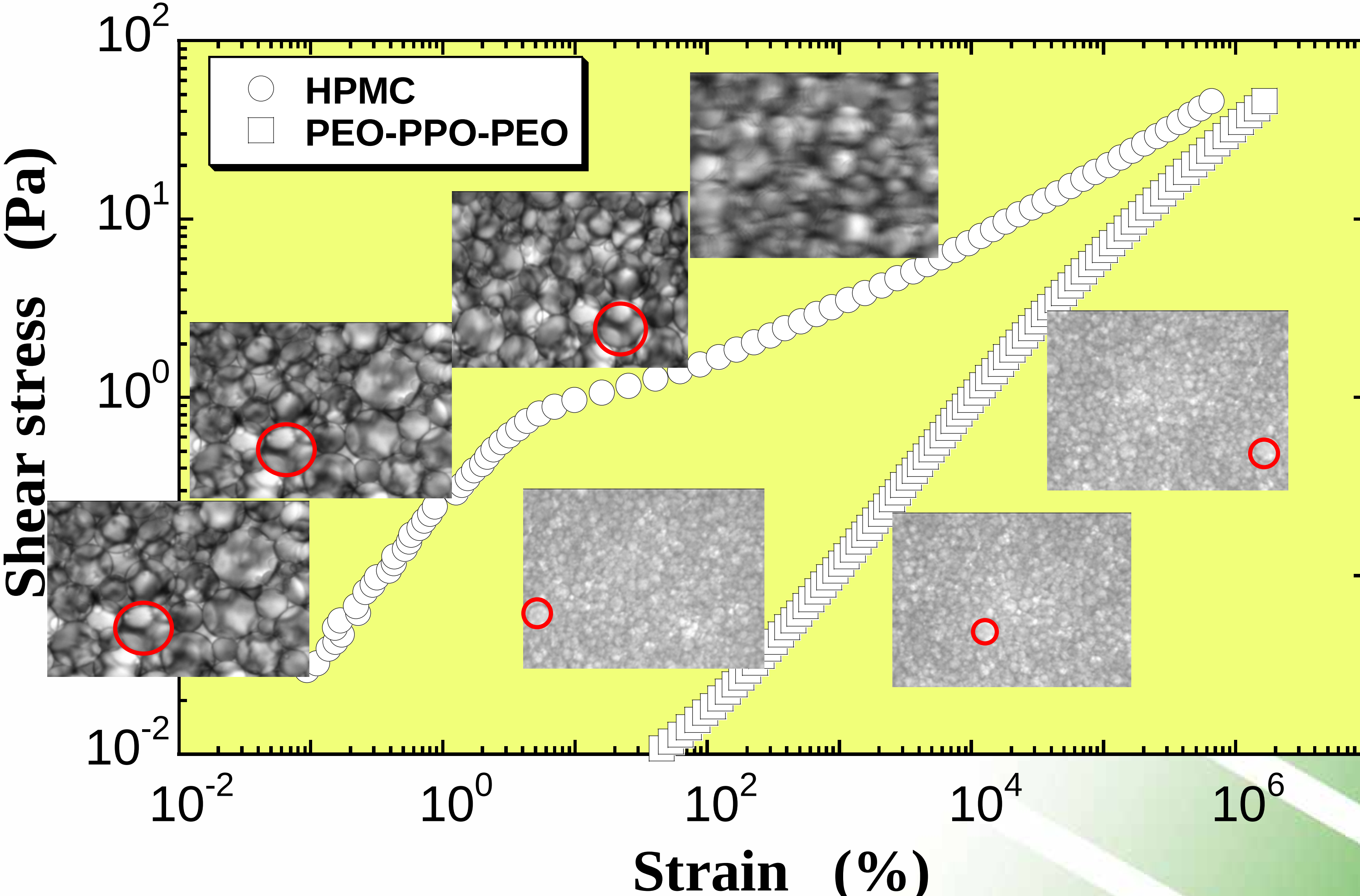
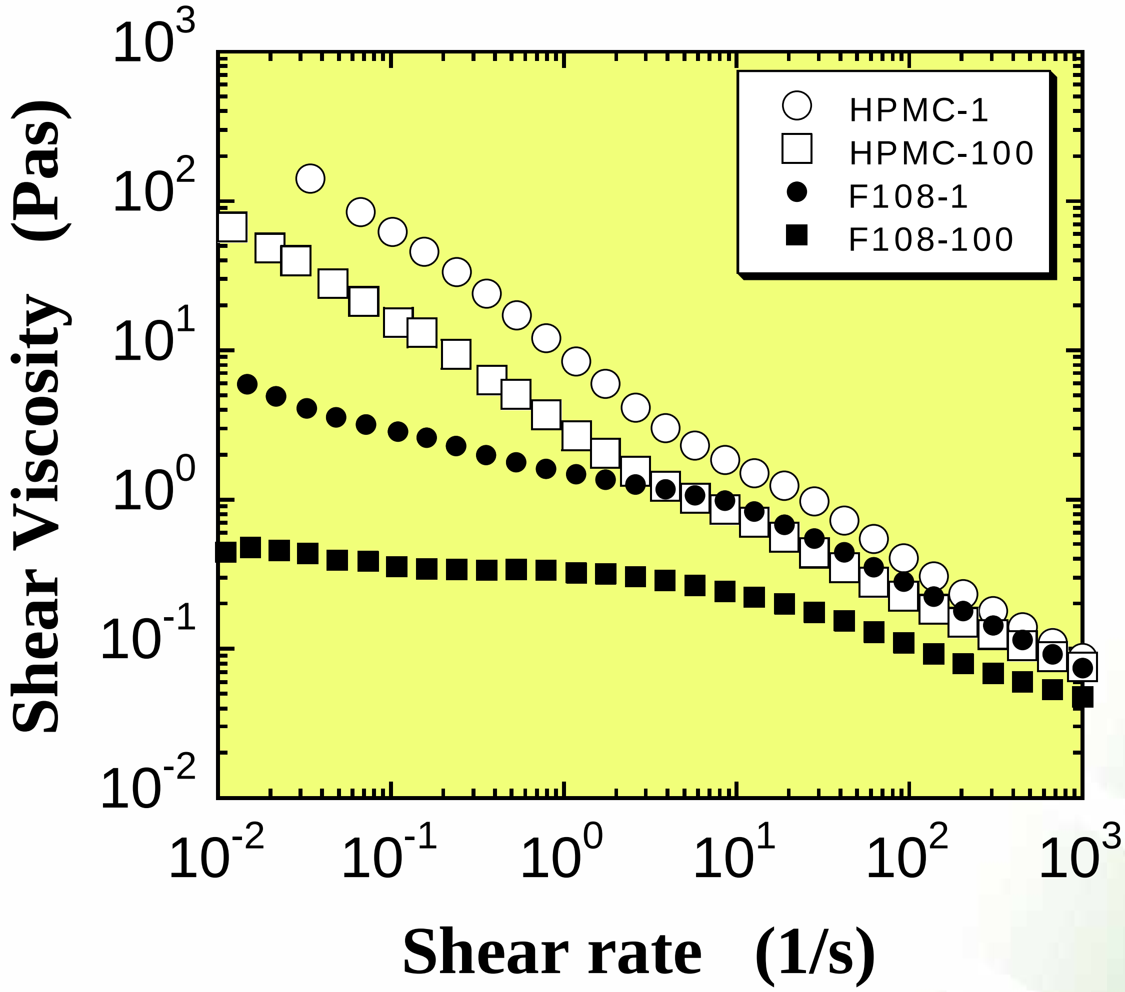
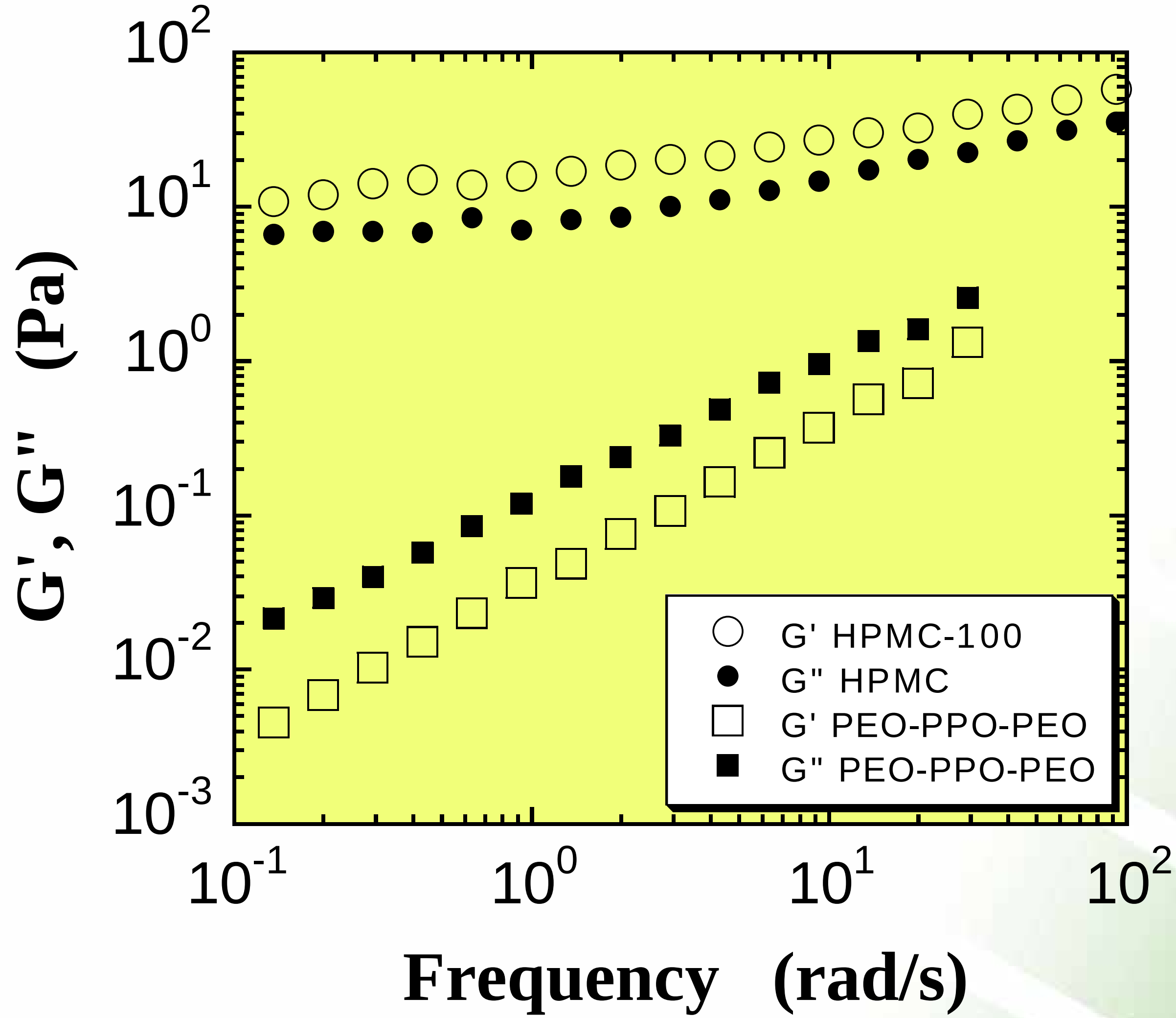
Rheoscope1



Stress-strain curves of the emulsions prepared by HPMC and PEO-PPO-PEO for 1 cSt silicone oil, together with the optical microscopic images of the corresponding emulsions at given strains. A red circle in each image indicates the same oil droplet.



Plots of shear viscosities of the emulsions prepared by HPMC (open symbols) and PEO-PPO-PEO (filled symbols) as a function of shear rate for different silicone oils:1 cSt (circles); 100 cSt (squares).



Plots of G’ (open symbols) and G” (filled symbols) of the emulsions prepared by HPMC (circles) and PEO-PPO-PEO (squares) as a function of frequency for 100 cSt silicone oil

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Comparison of the measured G’ and the calculated one of the emulsions prepared by HPMC for different silicone oils

Oil viscosity (cSt)	$D_{3,2}$ (μm)	Measured G’ at 1 rad/s (Pa)	Calculated G’ (Pa)
1	37.6	123	64.5
10	45.3	74.1	53.7
100	60.7	49.7	40.9
1000	85.9	34.2	31.5

Calculated G’ = $\phi_{eff}(\phi_{eff} - \phi_c)2\sigma_{in}/D_{3,2}$; $\phi_{eff} = \phi(1 + 3h/D_{3,2})$, where ϕ_c is the volume fraction of the random close-packing (0.64), σ_{in} is an interfacial tension (17.3 mN/m), ϕ is the volume fraction of the emulsion (0.72), and h is the adsorbed polymer layer thickness (20 nm).

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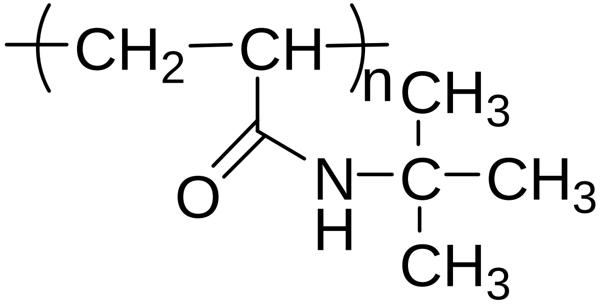
Emulsions prepared by PNIPAM

PNIPAM: PNIPAM-80 (Mw = 833 × 10^3, C* = 0.85 g/100 mL), PNIPAM-150 (1.54×10^6 , C* = 0.62 g/100 mL), PNIPAM-1000 (1.01×10^7 , C* = 0.23 g/100 mL)



Silicone oil: KF96L-1; Kinetic viscosity = 1 cSt

Interfacial tension of oil/aqueous solution of PNIPAM = 12.3 mN/m

Preparation of emulsions: 10g of silicone oil were agitated with 20g of aqueous solutions of PNIPAM with different concentrations for 30 min at 8000 rpm and 25 ^{o}C.

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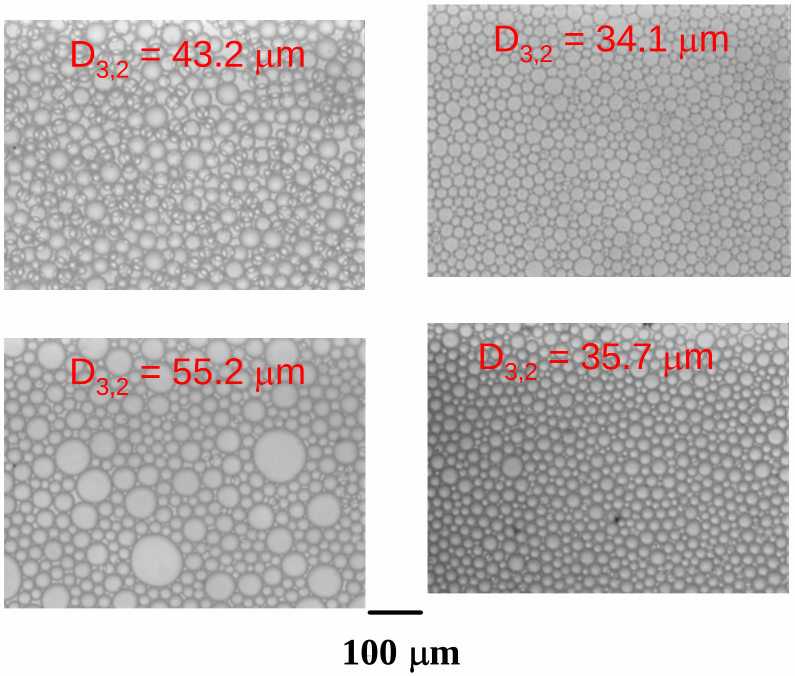
Characteristics of the emulsions prepared by PNIPAM

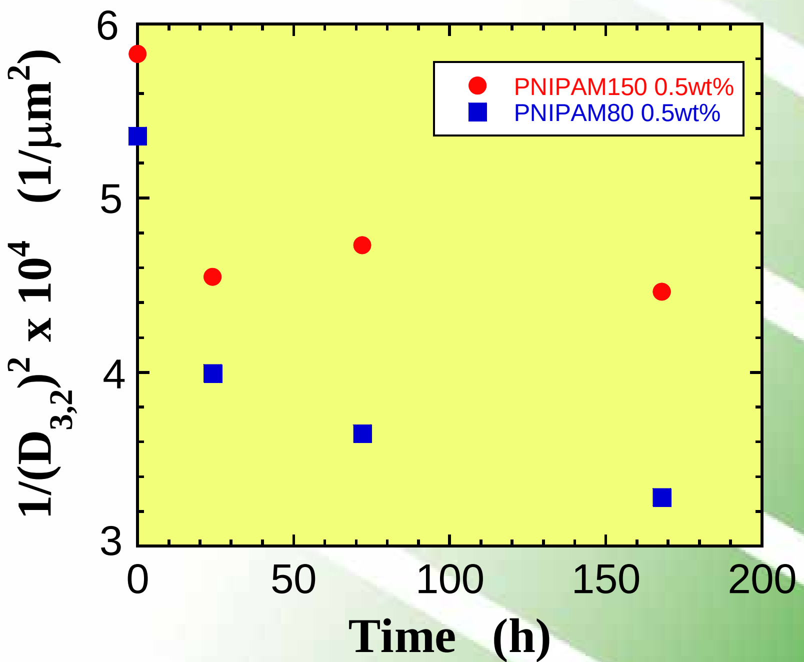
	0.5g/100 mL PNIPAM-80	1.3g/100 mL PNIPAM-150
Just	$D_{3,2}$ = 43.2 μm	$D_{3,2}$ = 34.1 μm
1 week	$D_{3,2}$ = 55.2 μm	$D_{3,2}$ = 35.7 μm



Adsorbed amount of PNIPAM = 1.17 mg/g

Adsorbed amount of PNIPAM = 1.78 mg/g

Deminiere et al. predicted a linear decreasing relationship between the reciprocal of square of the droplet size and the evolution time



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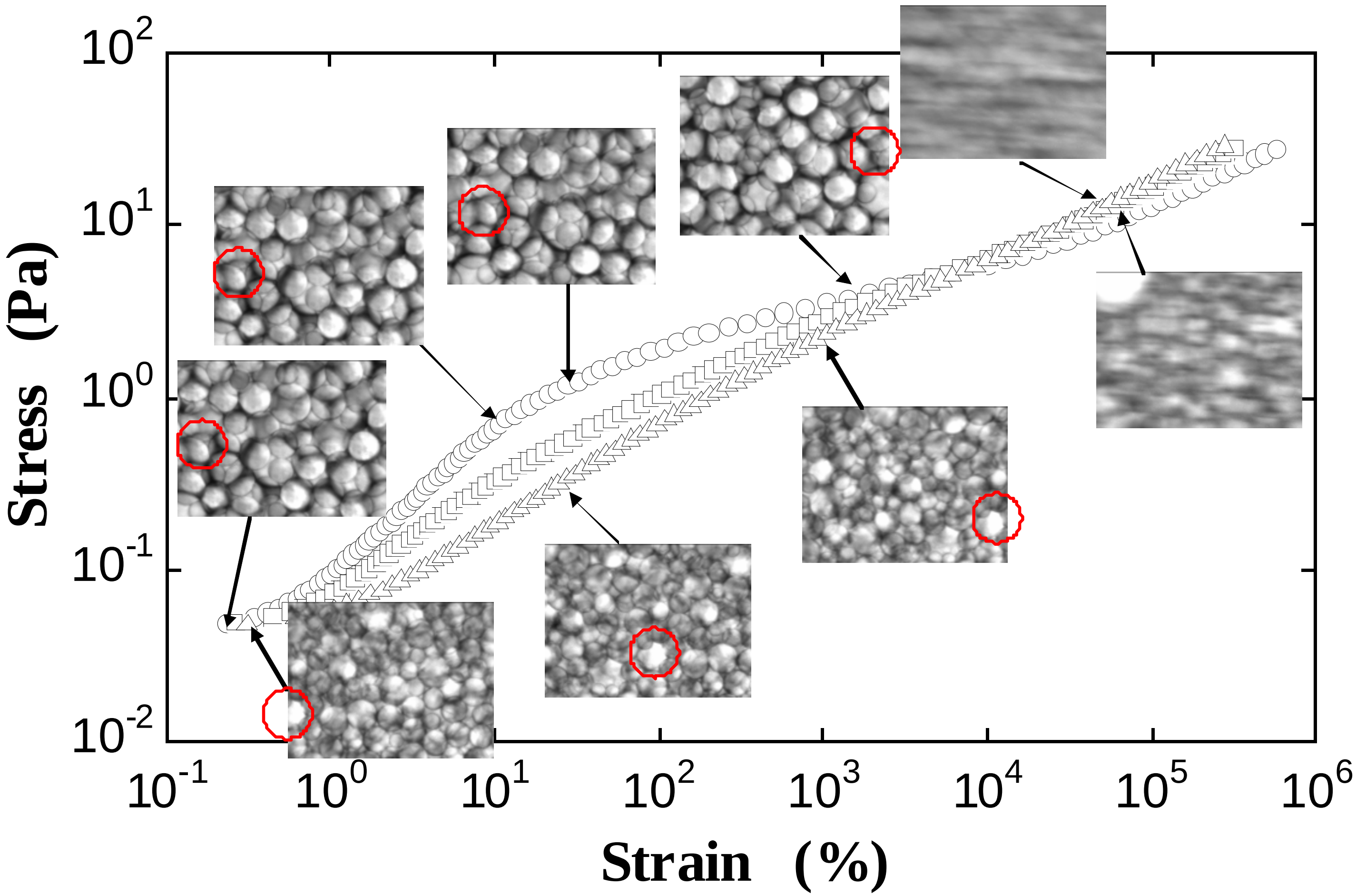
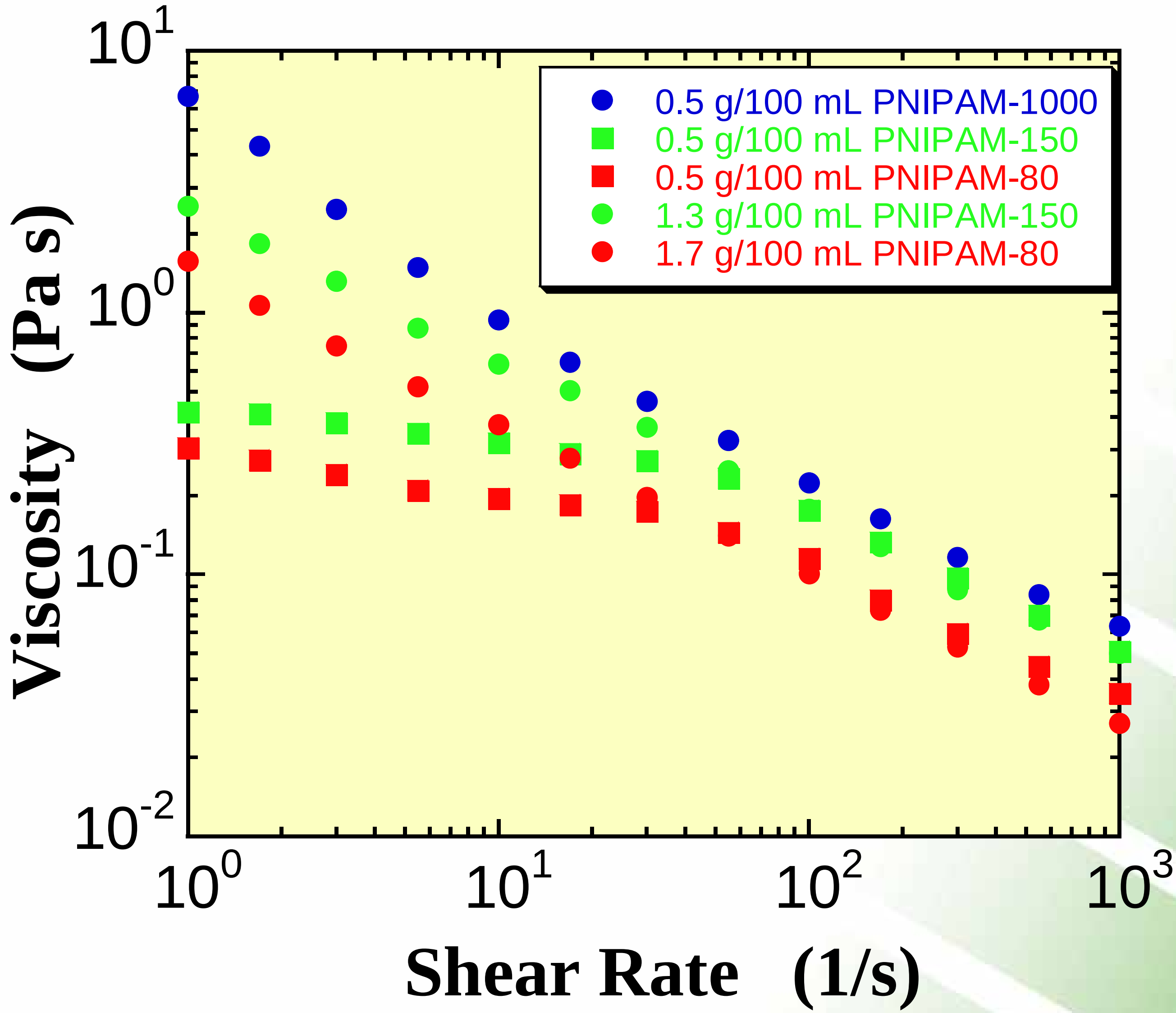


Stress-strain curves of the emulsions prepared by 1.7 g/100 mL PNIPAM-80 (△), 1.3 g/100 mL PNIPAM-150 (□), and 0.5 g/100 mL PNIPAM-1000 (○), together with the optical microscopic images of the corresponding emulsions at given strains. A red circle in each image indicates the same oil droplet. The respective PNIPAM concentrations correspond to 2C*.

Shear viscosities of the emulsions prepared by PNIPAM



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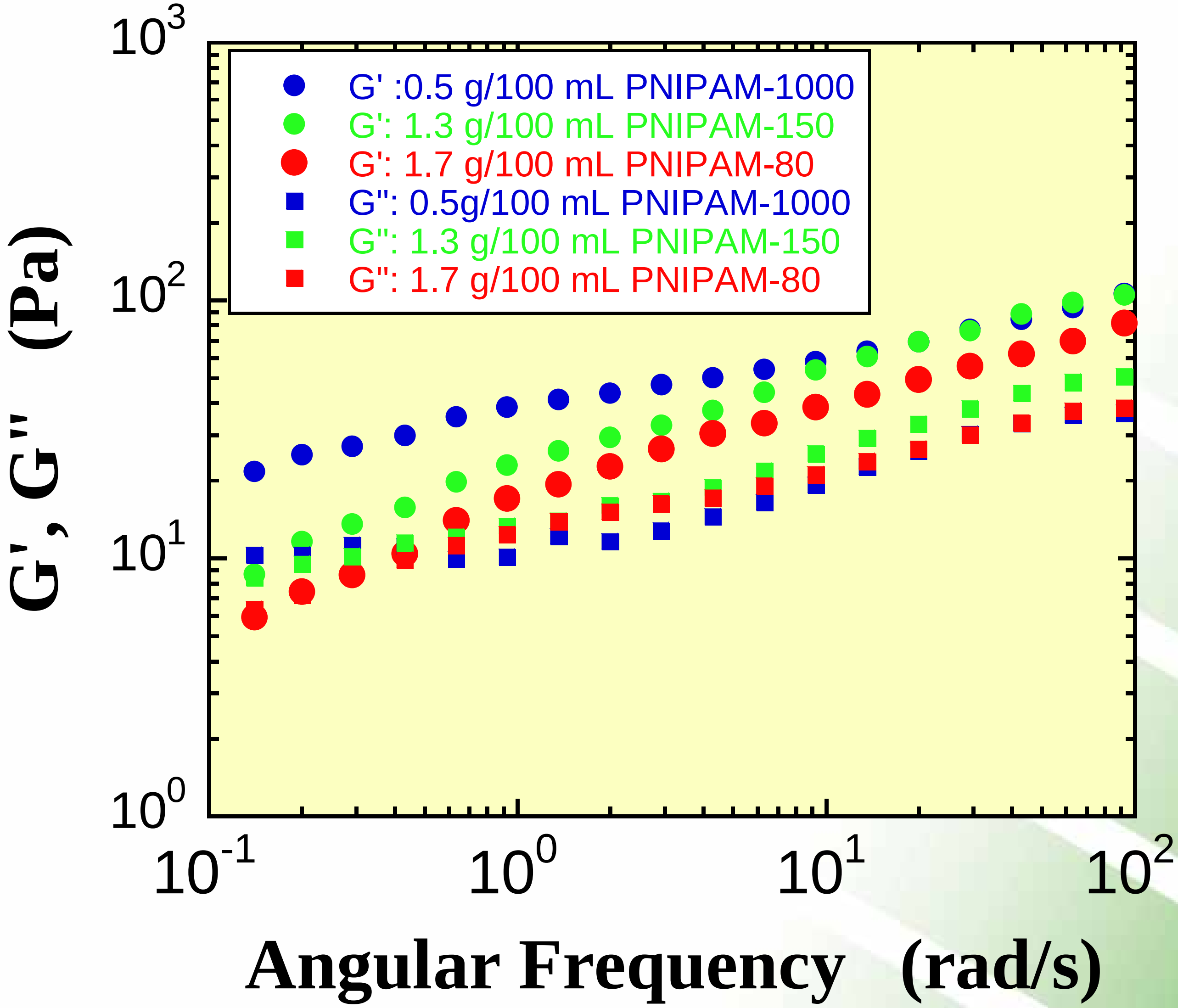
Dynamic moduli of the emulsions prepared by PNIPAM



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Conclusions for the emulsions prepared by polymers

1. HPMC, PEO-PPO-PEO, and PNIPAM are useful to prepare O/W emulsions.

2. The emulsions prepared by HPMC showed solidlike visco-elastic responses, whereas the emulsions prepared by PEO-PPO-PEO indicated liquidlike viscoelastic behavior. Moreover, the simultaneous optical microscopic observation showed that the emulsions stabilized by HPMC do not flow below the yield stress and beyond the yield stress the movements of oil droplets occur first.

3. The emulsions prepared at twice C* of PNIPAM showed solidlike viscoelastic responses. On the other hand, below C* the emulsions cause coalescence.

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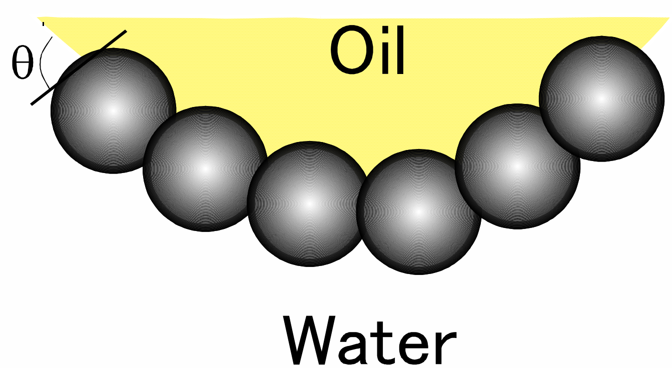
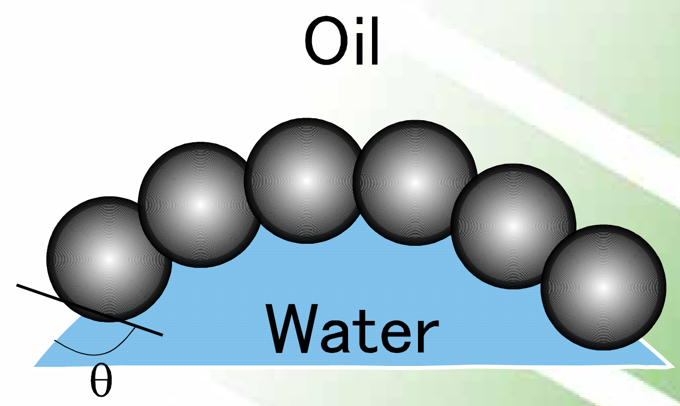
Pickering emulsions

Emulsions stabilized by solid particles are well-known as Pickering emulsions. The solid particles were ranged from inorganic materials to organic ones. The contact angle θ between oil-water interface is an important parameter to determine the type of Pickering emulsion.





R. J. G. Lopetinsky, J. H. Maliyah, and Z. Xu, in *Colloidal Particles at Liquid Interfaces*, eds. B. B. Binks and T. S. Horozov, Cambridge Univ. Press, p. 186 (2006).

Bilayer Stabilization

Bridging by a single layer

2-D network

Domains of particles

3-D network

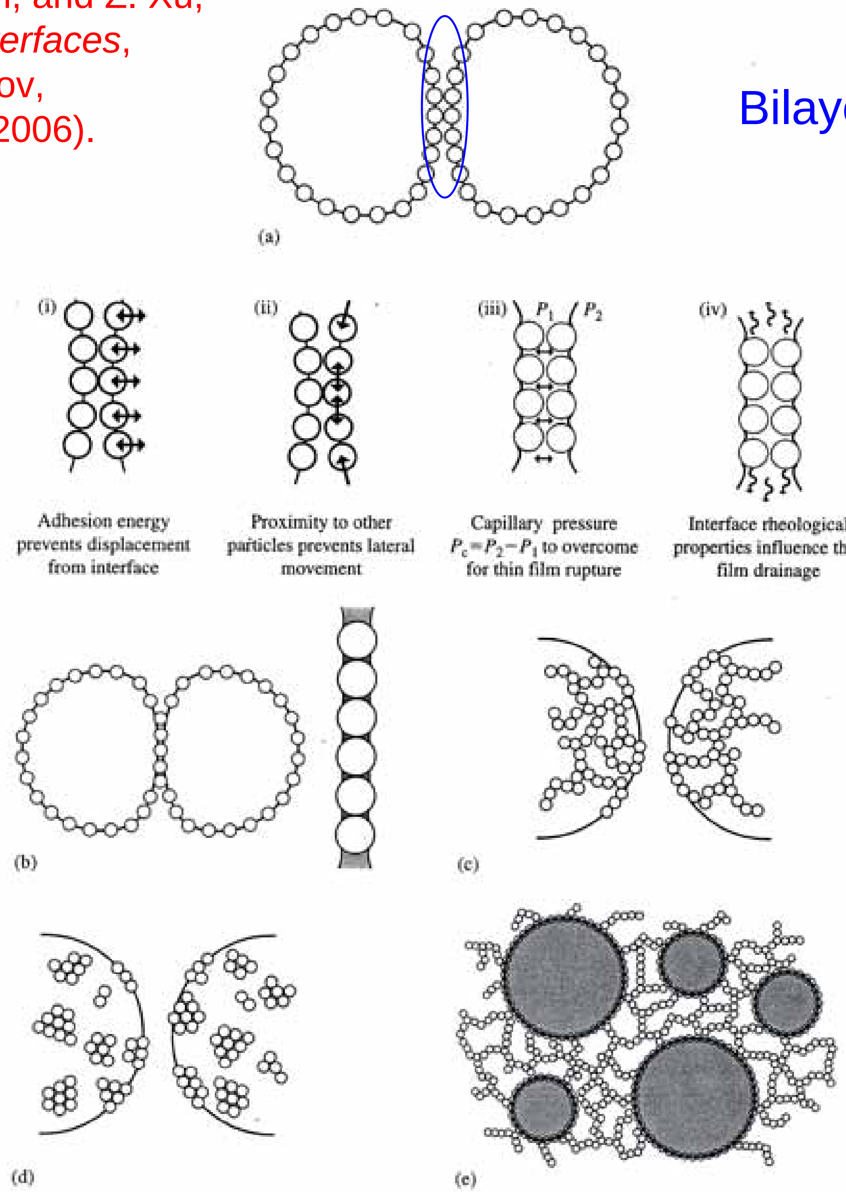


Figure 6.4 Possible configurations of particles in solids-stabilized emulsions, (a)–(e), and the underlying mechanisms responsible for stability (i)–(iv).

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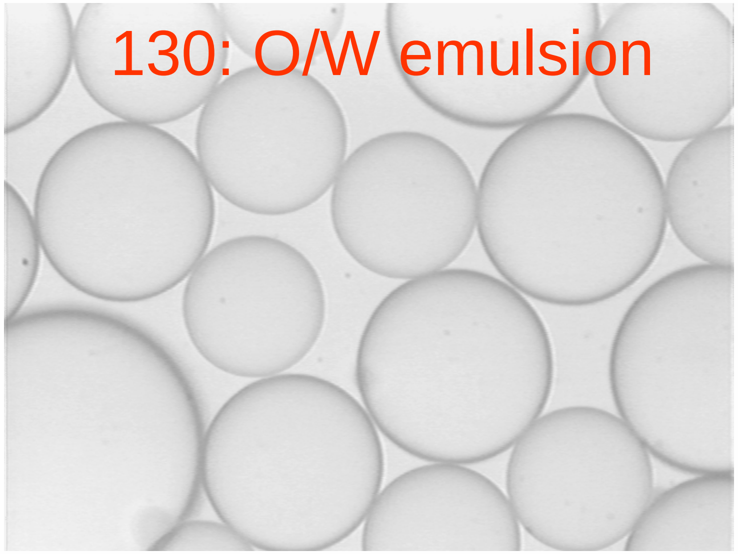
Emulsions stabilized by silica particles

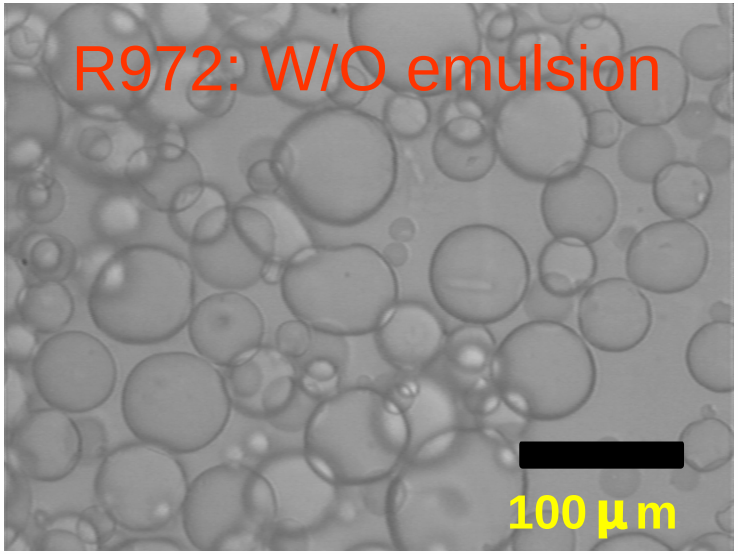
Aerosil-130: specific area = 130 m^2/g, silanol density = 2.5/nm^2
Aeosil-R972: specific area = 110 m^2/g, silanol density = 0.2/nm^2

Silicone oil: KF96L-1; Kinetic viscosity of 1 cSt

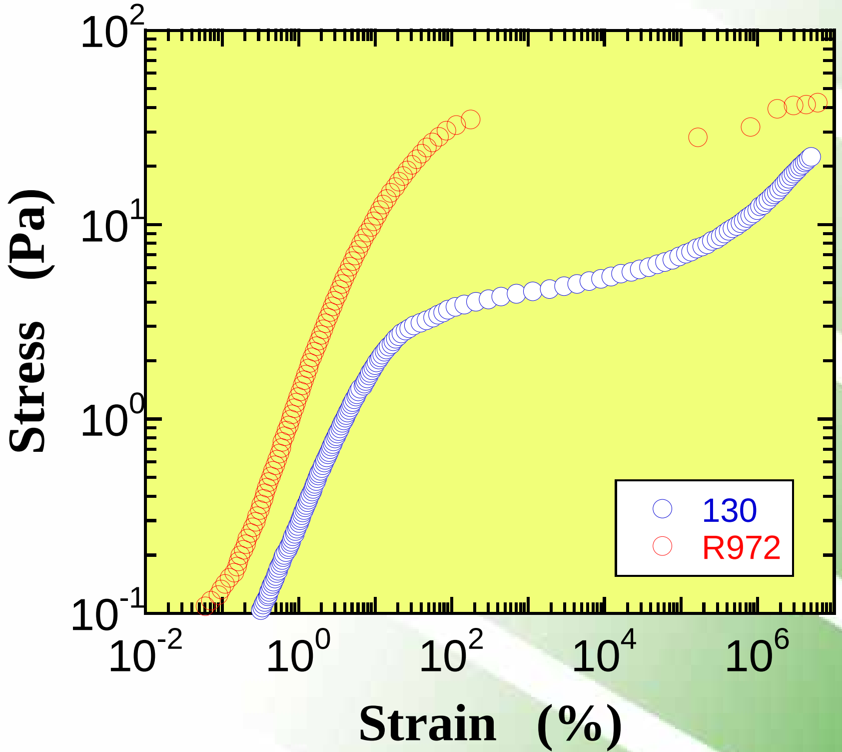
Preparation of emulsions: 15 g of silicone oil were mixed with 30 g of water dispersions with 0.45g of Aeosil-130; 10 g of silicone oil dispersions with 0.3g of Aerosil-R972 were agitated with 20g of water for 30 min at 8000 rpm and 25 ^oC.

Emulsions prepared by Aerosil silica particles





Stress-strain curves



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Emulsions prepared by silica particles pre-adsorbed HPMC

Emulsifiers: Aerosil-130 particles pre-adsorbed by HPMC (Mw = 380$\times10^3$, C* = 0.172 g/100 mL) below at the plateau region of adsorption isotherm of HPMC (0.14 g/g) were washed out to remove the free HPMC.

Silicone oil: KF96L-1; Kinetic viscosity of 1 cSt

Preparation of emulsions: 15 g of silicone oil were mixed with 30 g of water dispersions with 0.45 g of Aeosil-130 pre-adsorbed HPMC were agitated for 30 min at 8000 rpm and 25 ^{o}C.

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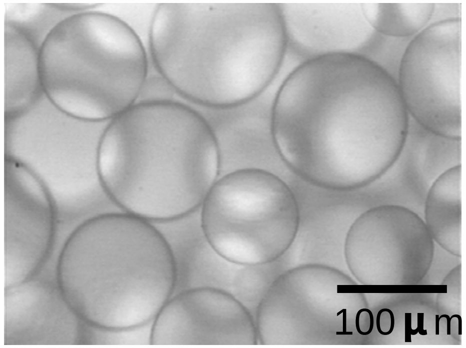
Optical microscopic images of the emulsions

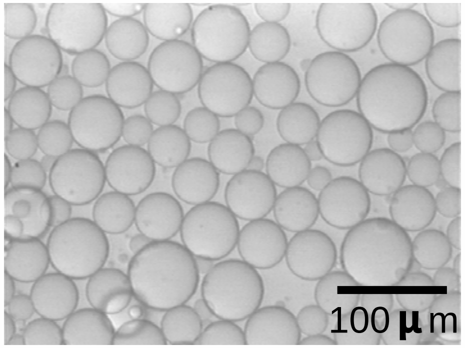
Silica only



$D_{3,2}$ = 113 μm

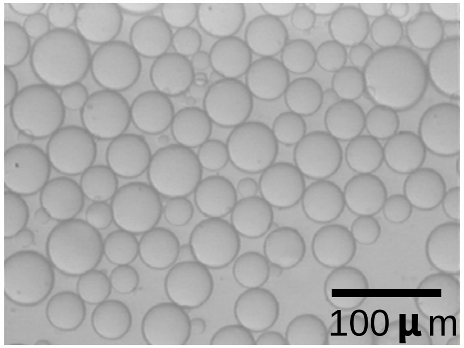
HPMC only

HPMC：0.015g



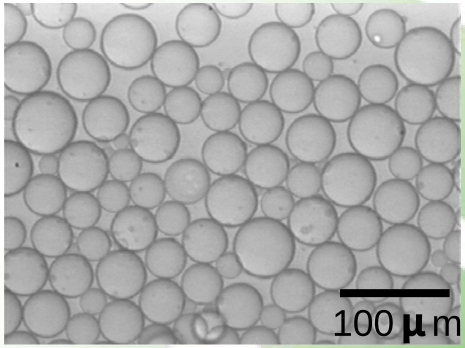
$D_{3,2}$ = 50,4 μm

HPMC：0.030g



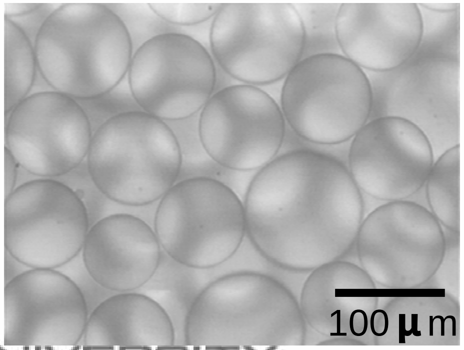
$D_{3,2}$ = 46.7 μm

HPMC：0.050g

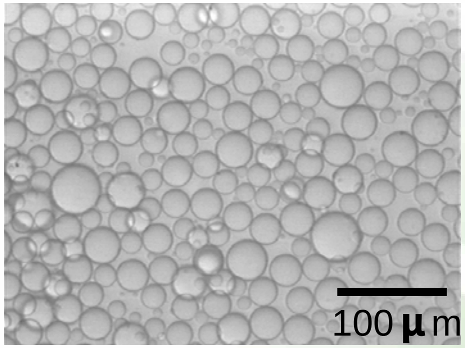


$D_{3,2}$ = 41.1 μm

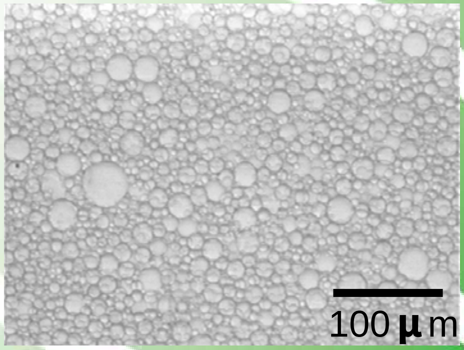
Silica pre-adsorbed HPMC



$D_{3,2}$ = 81.4 μm



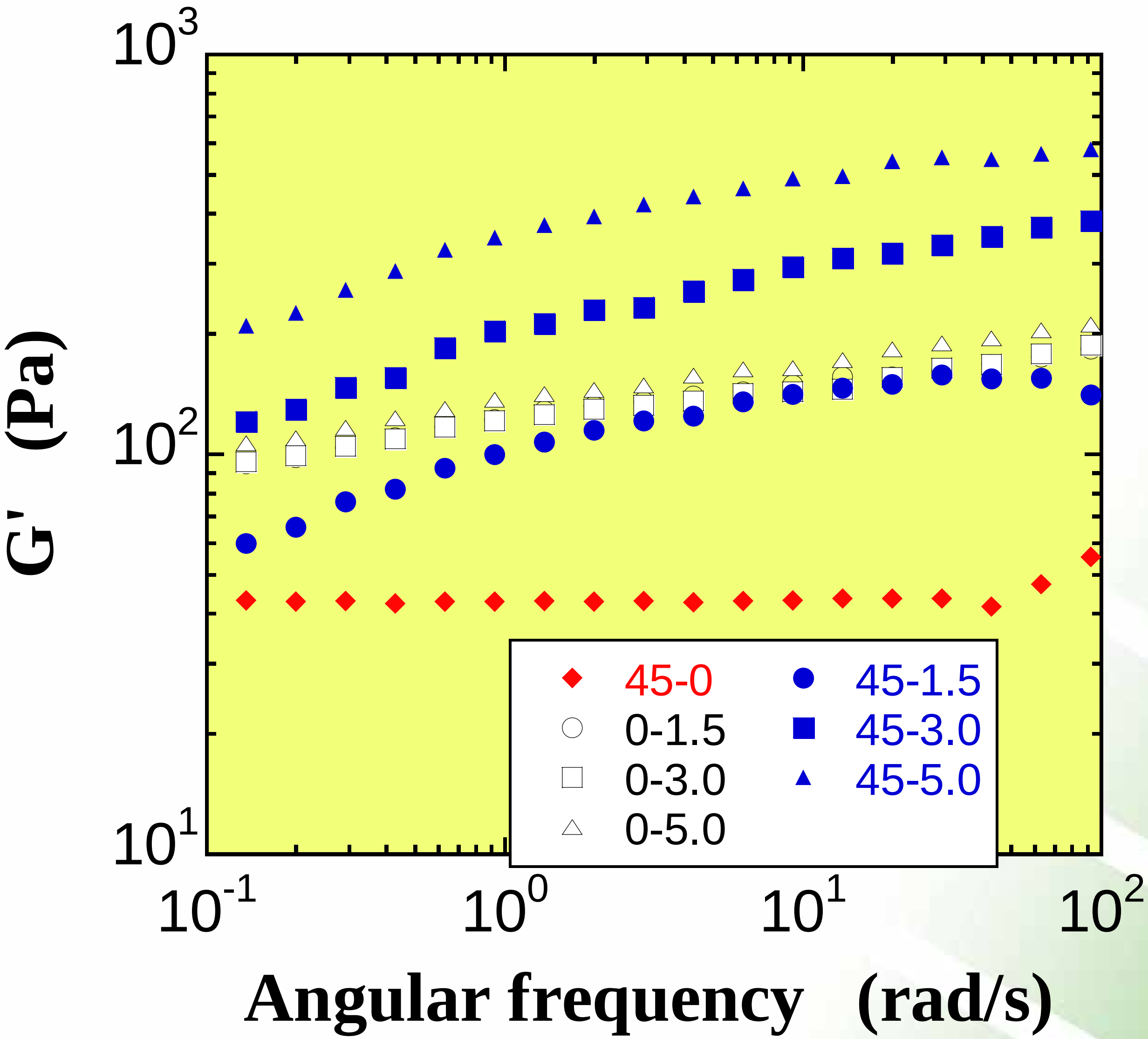
$D_{3,2}$ = 27.0 μm



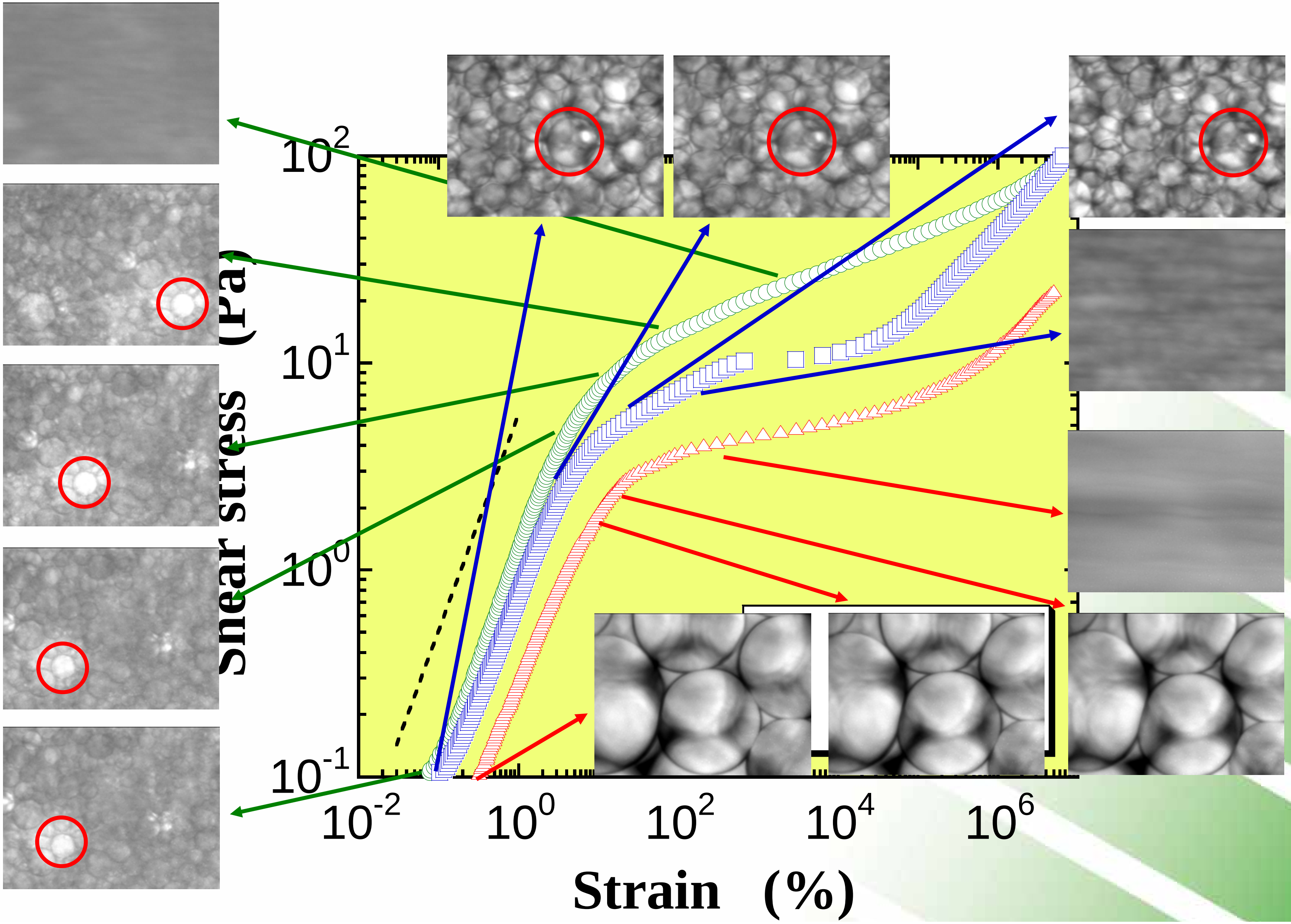
$D_{3,2}$ = 14.5 μm

Characteristics of the emulsions prepared by the hydrophilic silica particles pre-adsorbed HPMC

HPMC (g)	Silica (g)	ϕ_{rel}	A_d (mg/g)	$D_{3,2}$ (μm)	σ_{in} (mN/m)
0.015	0.0	1.0	1.0	50.4	17.3
0.030	0.0	1.0	2.0	46.7	17.3
0.050	0.0	1.0	3.3	41.1	17.3
0.0	0.45	0.8	0.0	113	36.8
0.015	0.45	0.95	17.2	81.4	36.6
0.030	0.45	0.89	22.4	27.0	36.3
0.050	0.45	0.82	30.4	14.5	20.5



G’ of the emulsions prepared by Aerosil-130 pre-adsorbed HPMC, HPMC, and Aerosil-130



Stress-strain curves of the emulsions prepared by silica (△)、HPMC (□) and silica pre-adsorbed by HPMC (○). HPMC = 0.050g

Emulsions prepared by Aerosil-130 and Aerosil-R972 silica particles pre-adsorbed PNIPAM

Emulsifiers: Aerosil-130 and Aerosil-R972 particles pre-adsorbed by PNIPAM below at the plateau region of adsorption isotherm (0.12 g/g) of PNIPAM (Mw = 492×10^3 and C* = 1.12 g/100 mL) were washed out to remove the free PNIPAM.

Silicone oil: KF96L-1; Kinetic viscosity of 1 cSt

Preparation of emulsions: 10 g of silicone oil were mixed with 20 g of water dispersions with 0.30g of Aeosil-130 and Aerosil-R972 pre-adsorbed PNIPAM were agitated for 30 min at 8000 rpm and 25 ^{o}C.

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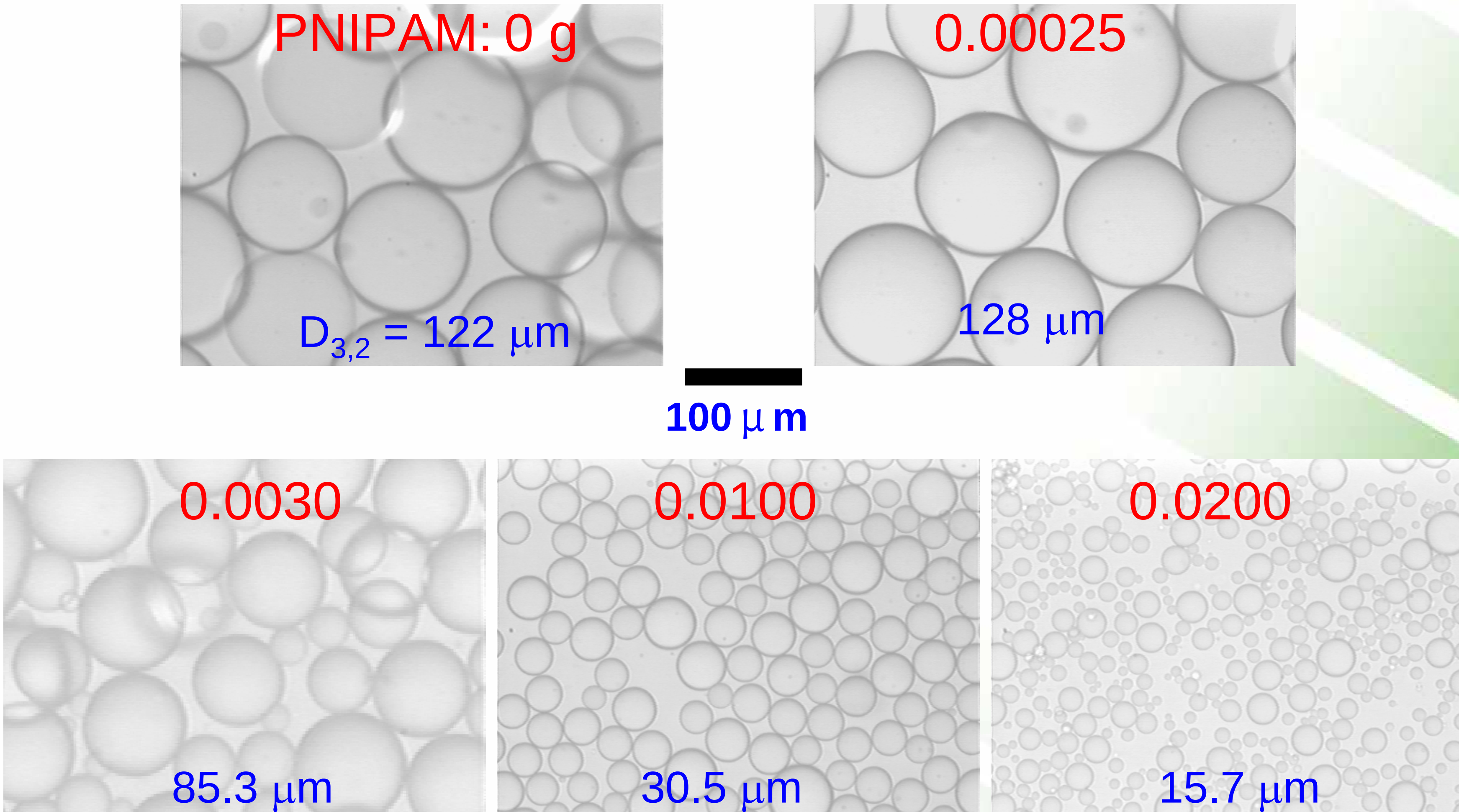
Optical microscopic images of the emulsions prepared by Aeosil-130 pre-adsorbed PNIPAM



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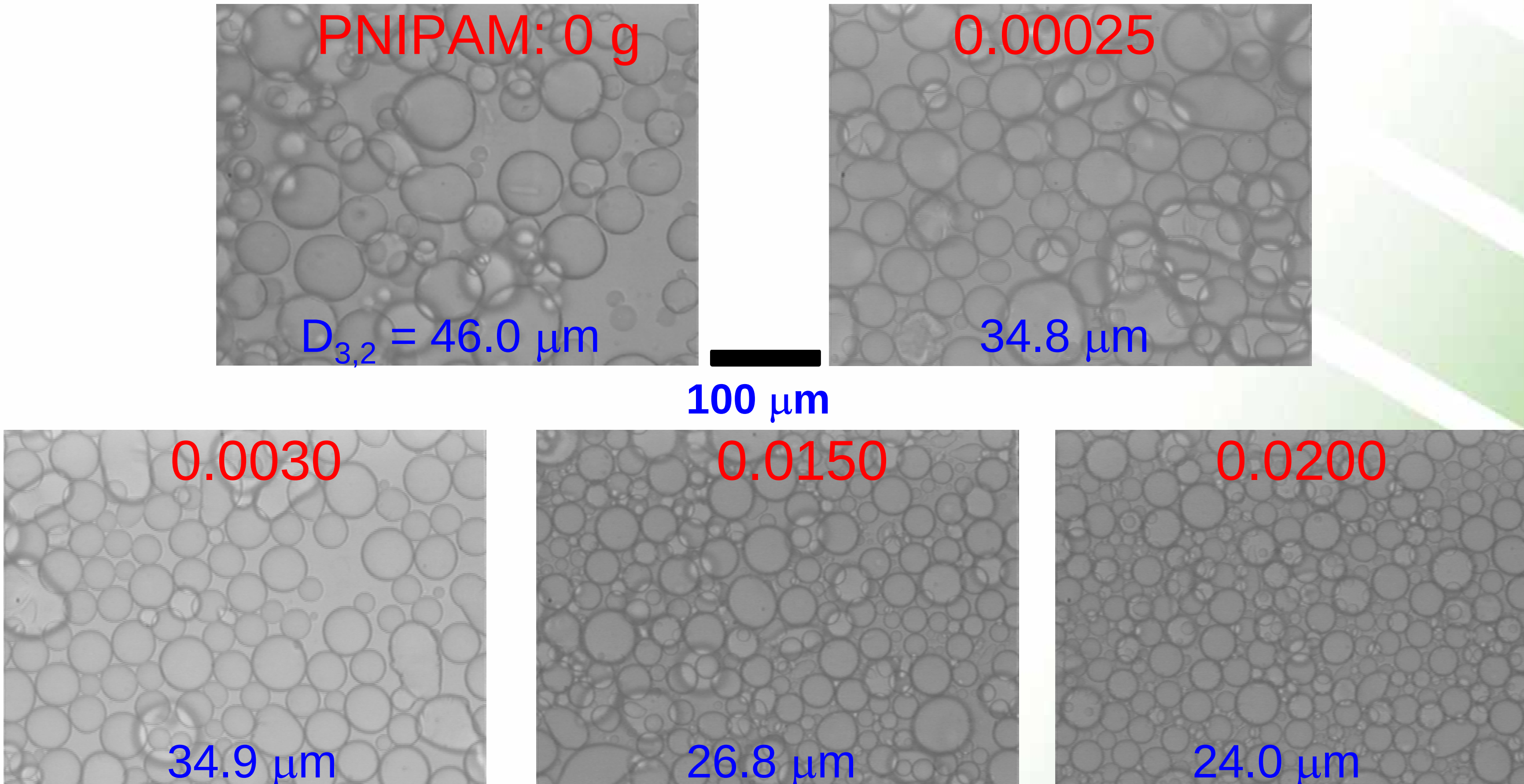
Optical microscopic images of the emulsions prepared by Aeosil-R972 pre-adsorbed PNIPAM



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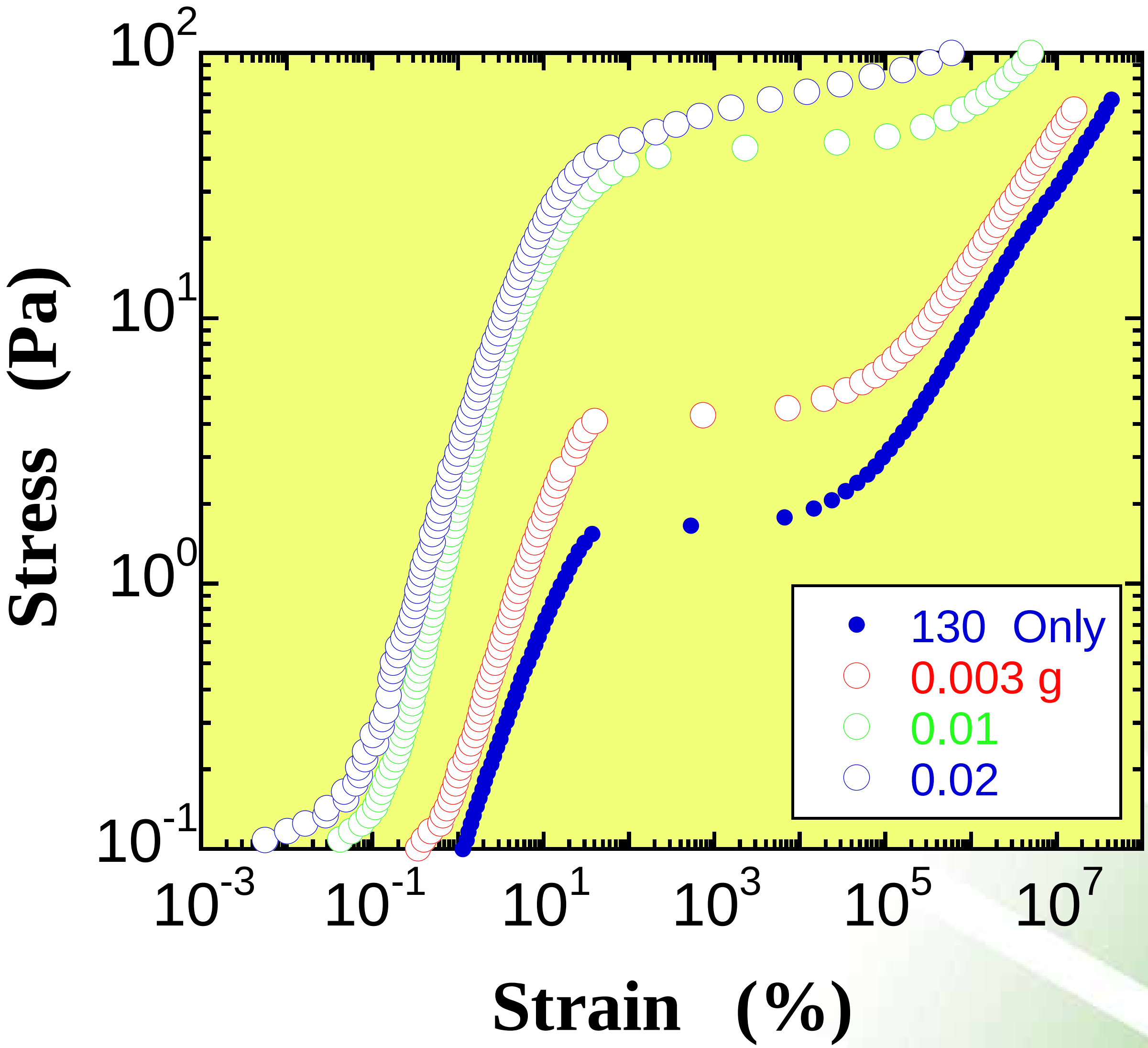
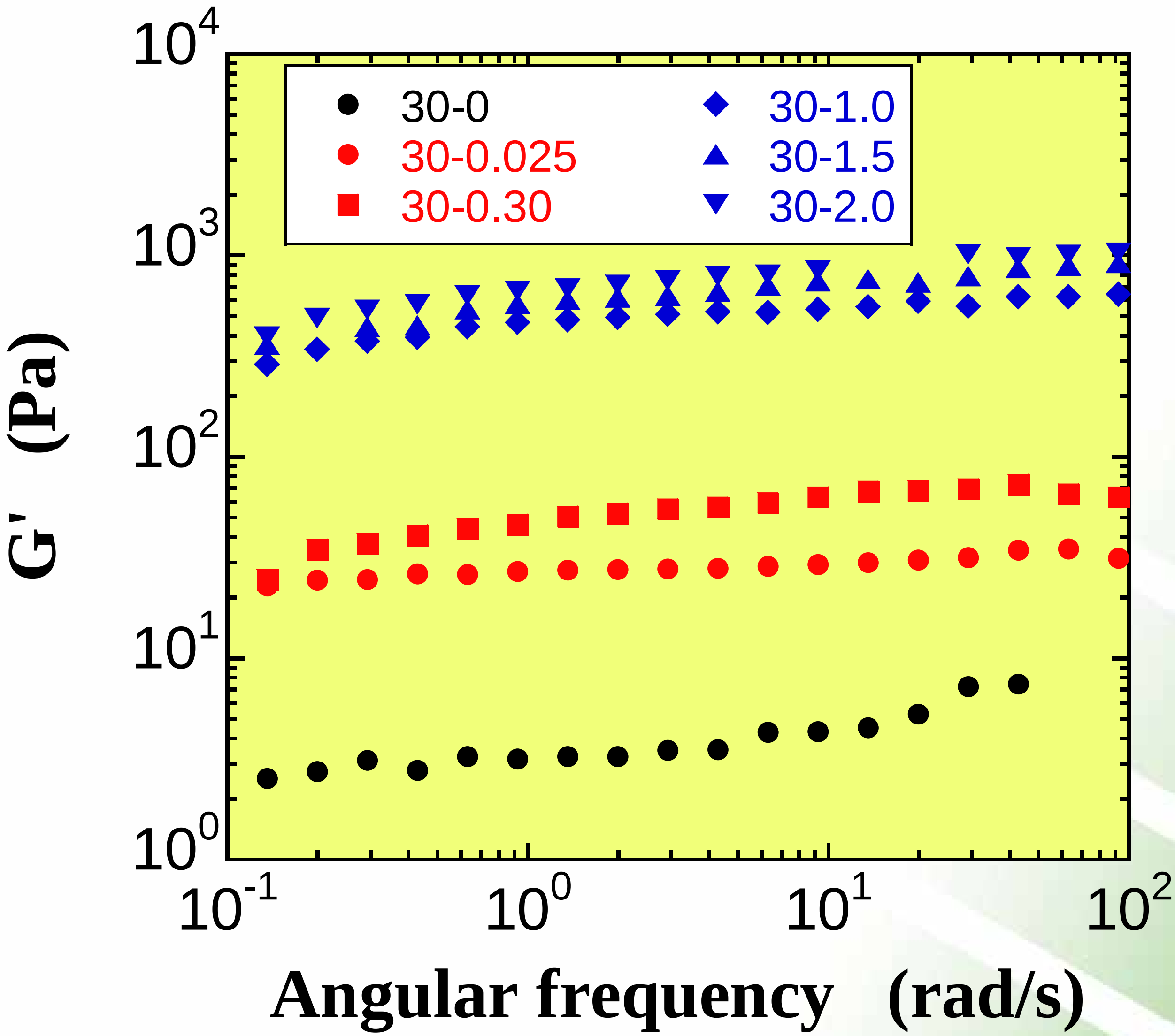
Characteristics of the emulsions prepared by the hydrophilic and hydrophobic silica particles pre-adsorbed PNIPAM

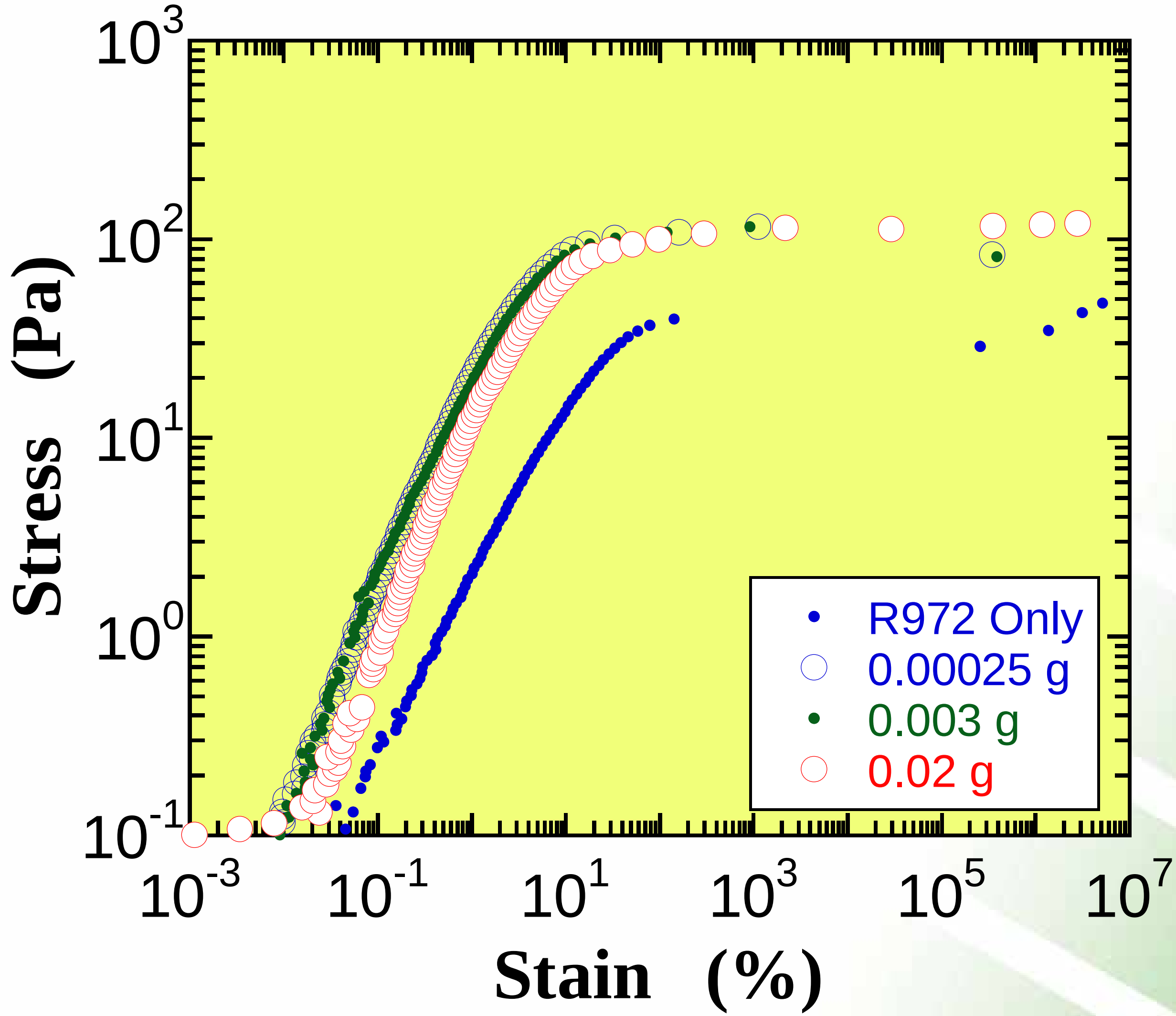
PNIPAM (g)	ϕ_{rel}	A_d (mg/g)	$D_{3,2}$ (μm)	ϕ_{rel}	A_d (mg/g)	$D_{3,2}$ (μm)
	Aerosil-130			Aeosil-R972		
0.0	0.72	0.0	122	1.00	15.0	46.0
0.00025	0.89	0.4	125	0.97	13.4	34.8
0.001	1.00	2.6	146	0.99	12.6	34.8
0.003	1.00	4.2	85.3	0.99	12.6	34.9
0.01	1.00	10.8	30.5	0.98	13.6.	34.8
0.015	1.00	14.6	19.3	1.00	19.2	26.8
0.02	1.00	17.9	15.7	0.82	26.8	24.0



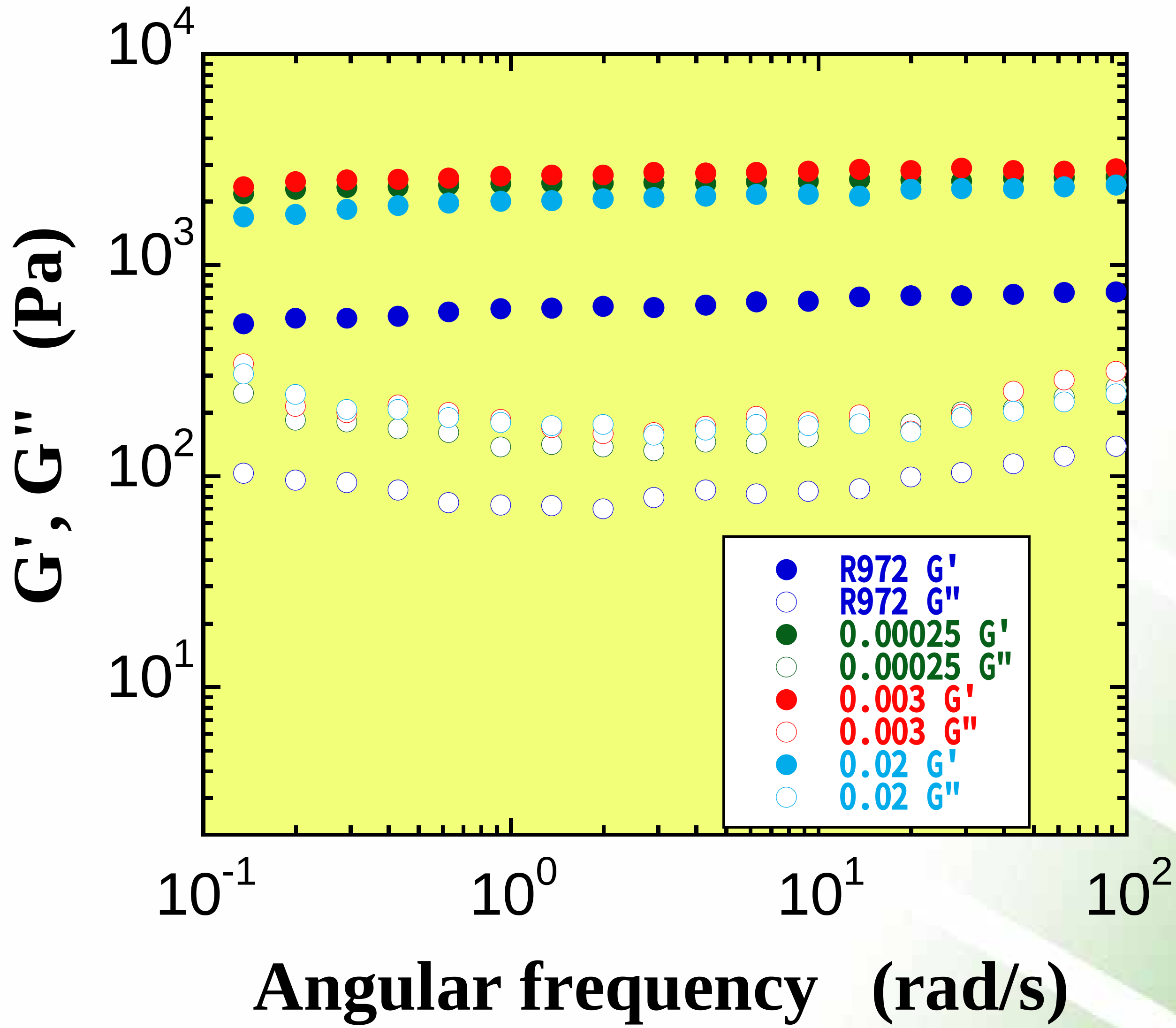
Stress-strain curves of the emulsions prepared by Aerosil-130 pre-adsorbed PNIPAM



G’ of the emulsions prepared by Aerosil-130 pre-adsorbed PNIPAM.



Stress-strain curves of the emulsions prepared by Aerosil-R972 pre-adsorbed PNIPAM



G’ and G” of the emulsions prepared by Aerosil-R972 pre-adsorbed PNIPAM

Conclusions for the emulsions prepared by silica particles pre-adsorbed polymers

1. Silica particles pre-adsorbed HPMC and PNIPAM are useful to prepare O/W emulsions.   The hydrophilic silica particles pre-adsorbed PNIPAM can fully emulsify silicone oil.

2. With an increase in the adsorbed amounts of polymers, the emulsions prepared the hydrophilic silica particles pre-adsorbed polymers showed a decrease in the size of oil droplets and an increase in the elastic response.

3. On the other hand, the emulsions prepared the hydrophobic silica particles pre-adsorbed polymers showed little changes in the size of oil droplets and the viscoelastic response.

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