Pickering Emulsion Approach: A Novel Strategy to Fabricate Waterborne Polyurethane with Enhanced Abradability and Water-Resistance Comparable to that of Solvent-based Coating

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2025.09

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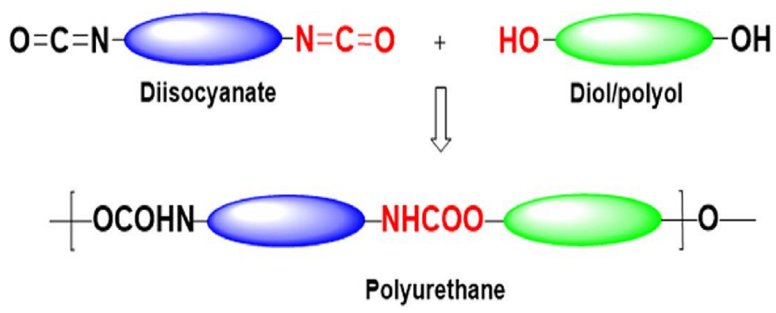
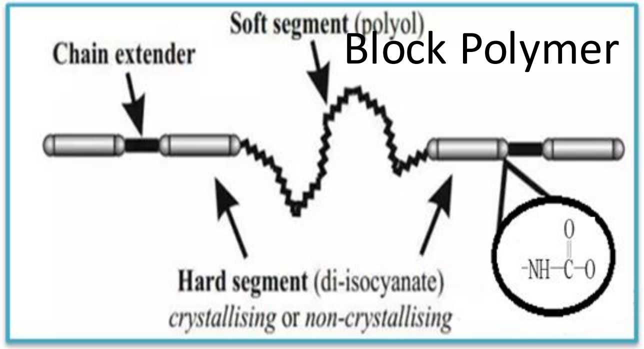
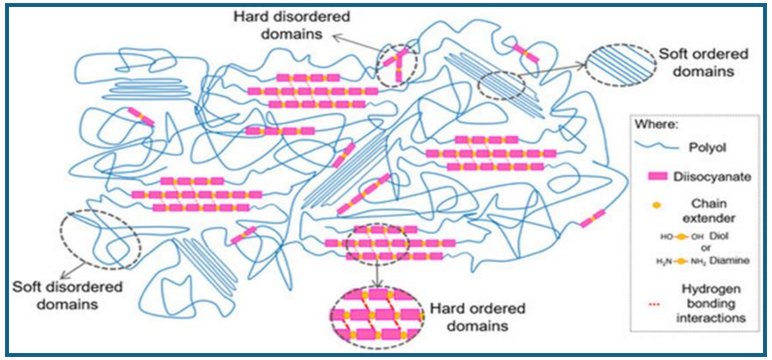
1. Background: Introduction of Polyurethane

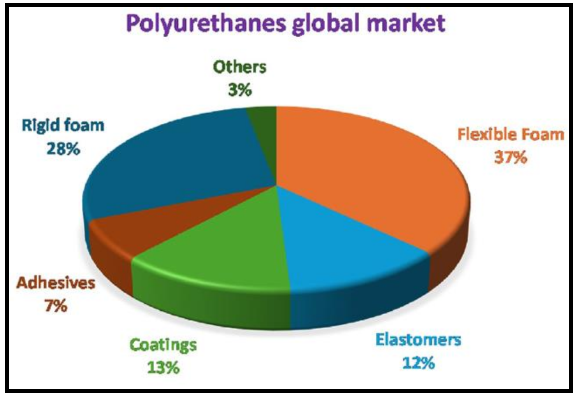
Polyurethane (PU) : ranked the sixth most manufactured worldwide polymers

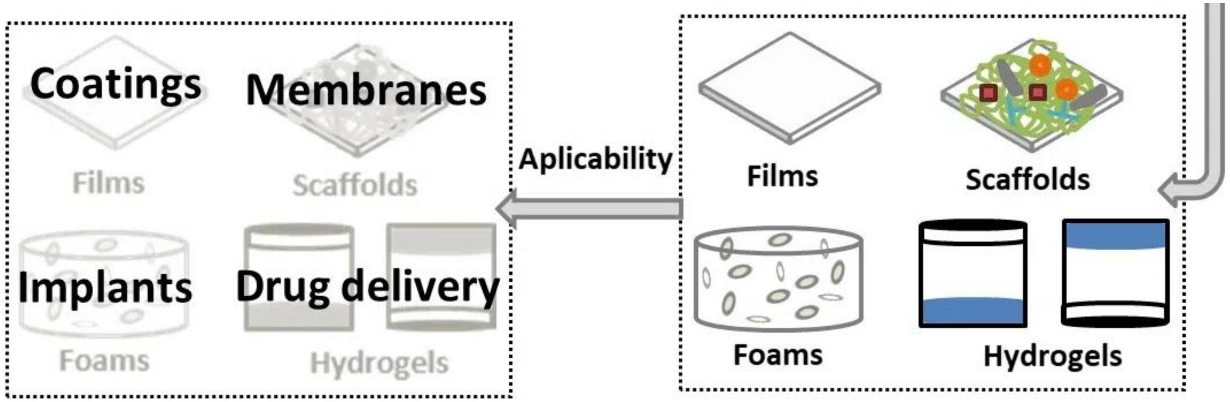
In leather industry, PU widely used both as leather coatings and as base material for synthetic leather







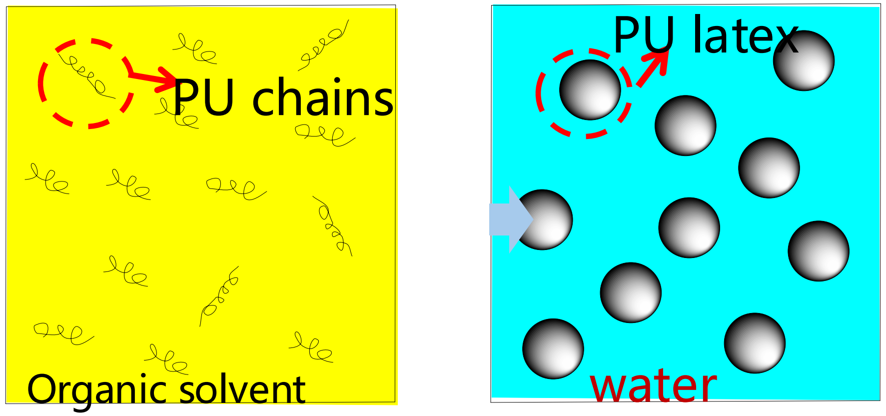




- ✓ **Variable raw material**
- ✓ **highly controllable molecular structure**
- ✓ **Micro-phase separated Structures**
- ✓ **Versatile properties**
- ✓ **Diverse application**

1. Waterborne Polyurethane (WPU) : green and safe alternative

Solvent PU (VOC emission) WPU

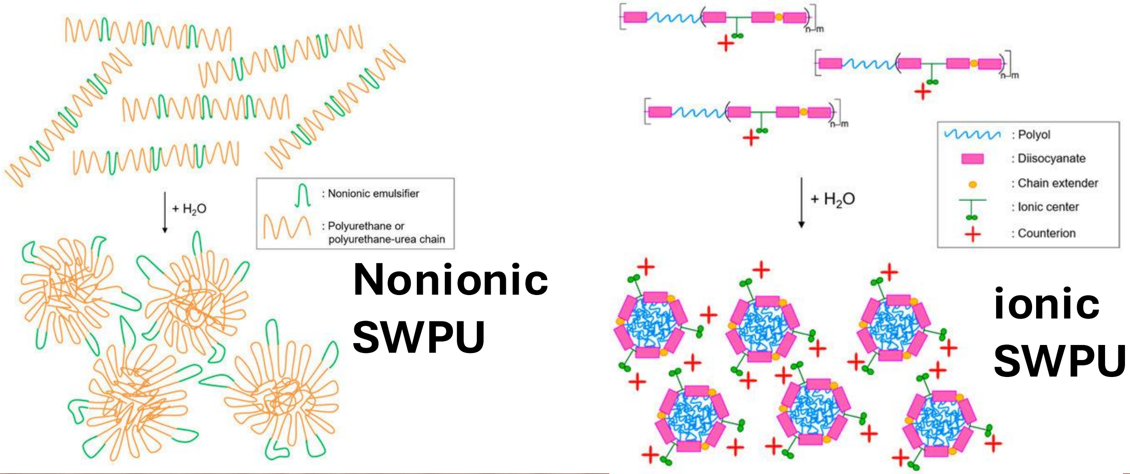


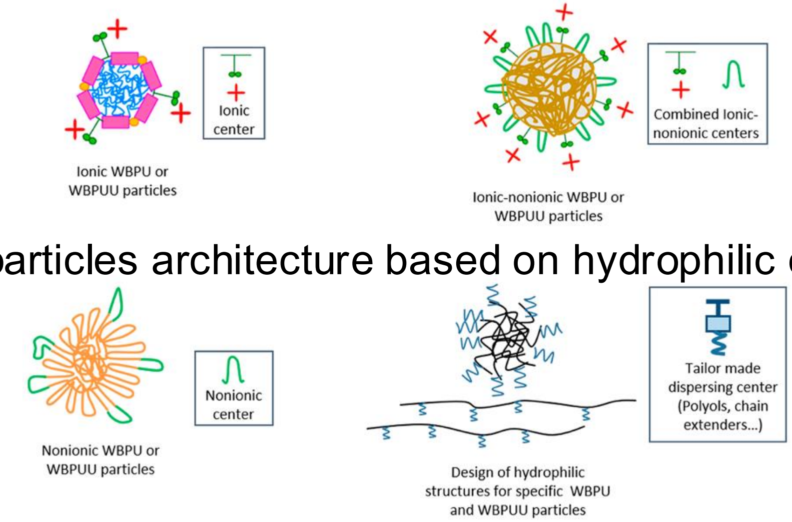
- ☐ External emulsification: addition of surfactants

- ☐ Internal emulsification (self-emulsifying SWPU)
  - covalently incorporating hydrophilic groups(internal emulsifiers) in PU
  - forms part of the polymeric chain
  - Commonly used for WPU

- ◆ Content of surfactants or hydrophilic groups : at a minimum level to get stable dispersions
  - ➢ reduced water resistance of PU films
  - ➢ Insufficient adhesion to substrate

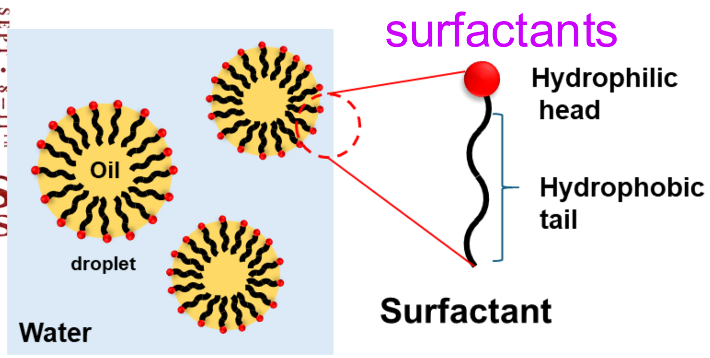
Latex particles formation of PU in water



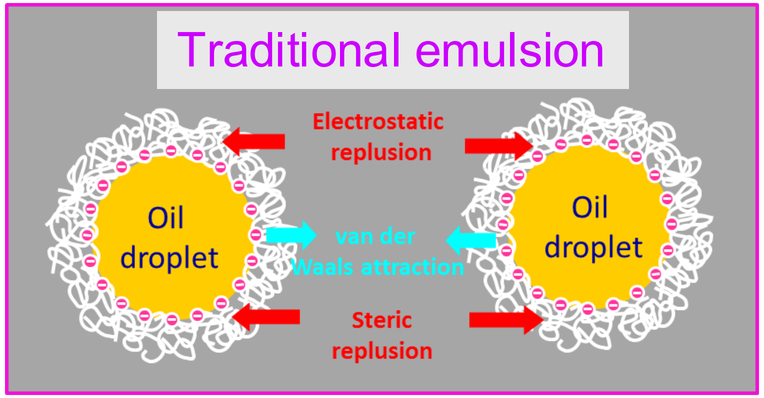


PU particles architecture based on hydrophilic center

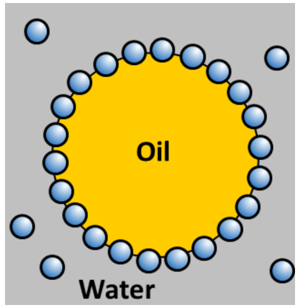
1. Pickering emulsion

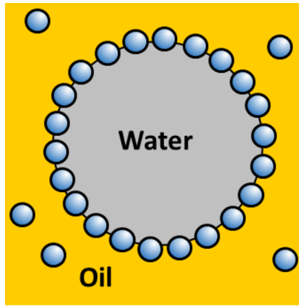


hydrophile-lipophile balance (HLB) value



Pickering emulsion： solid particles stabilized emulsion

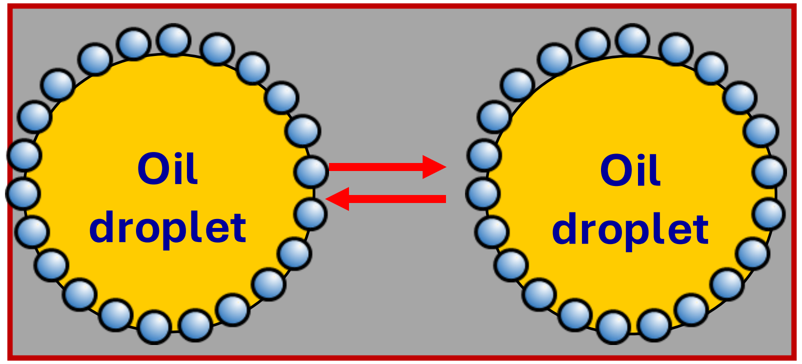




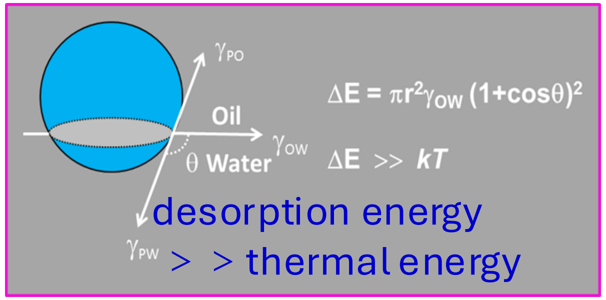
Particles size： nm - several submicrometer；irreversible absorption

Mechanism: formation of steric barrier by solid particles at interface

- ✓ superb stability > traditional emulsion
- ✓ All types of Particles (inorganic/organic, biobased..



Three phase contact angle

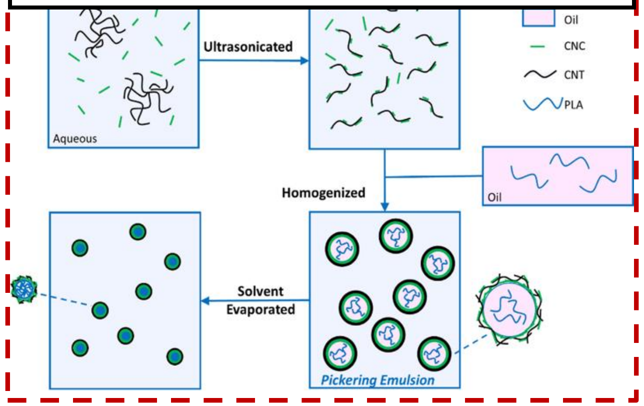


Can Pickering particles used for emulsifying PU ?

- ➢ act as stabilizer
- ➢ endow PU with useful characteristics
- ➢ Improving water resistance

?

The emulsifying of PLA (Polylactic Acid)

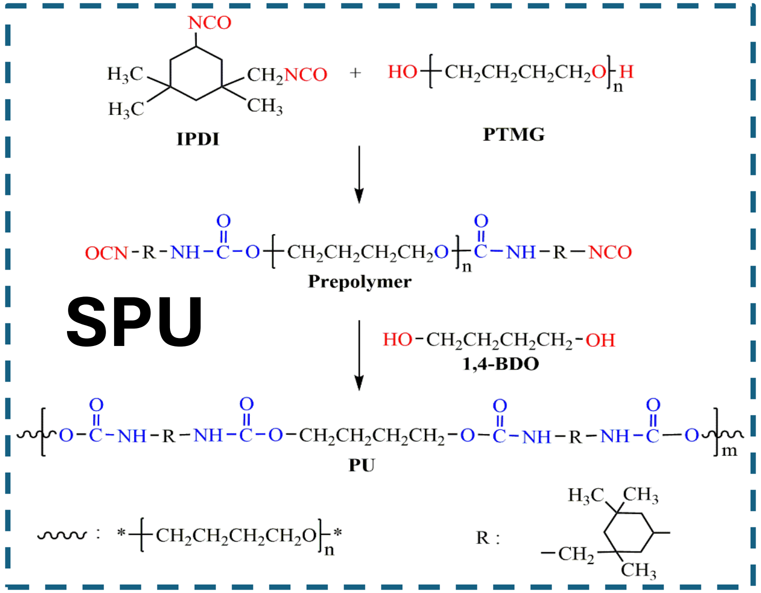


Li X, et al. Eur. Polym. J., 2019.

[1] Nakama Y. *Cosmetic Science and Technology*, 2017: 231-244. [2] Pickering S U. *Journal of the Chemical Society*, 1907, 91(0): 2001-2021.

2. Waterborne Polyurethane via Pickering emulsifying (PWPU)

SPU



PWPU

Silica particle (SiO_2)
Commonly used for Pickering emulsion

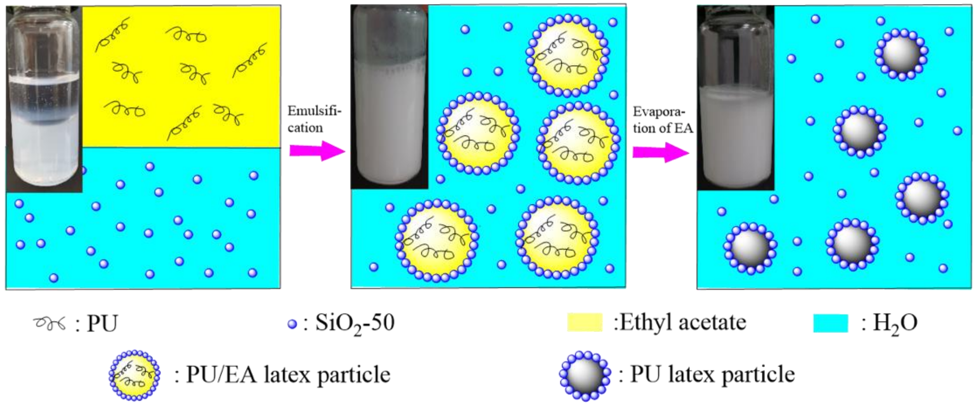
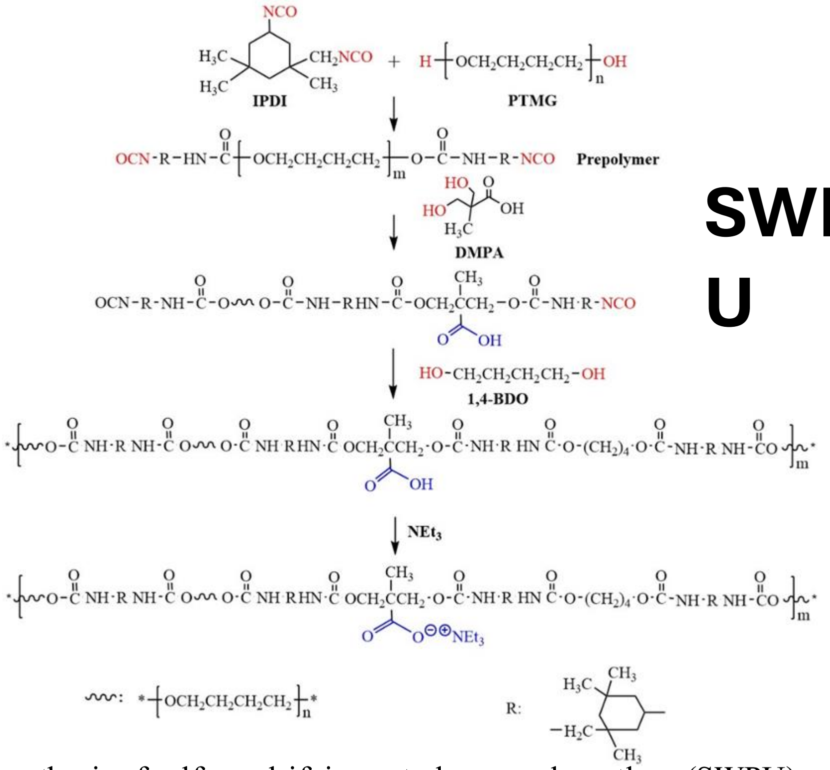


Table 2 The raw materials ratio to synthesize SPU, PWPU and SWPU

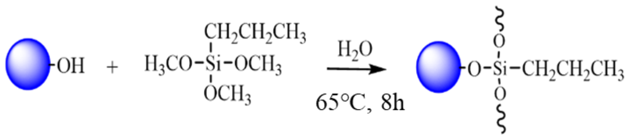
Sample	Solvent or emulsify method	IPDI	PTMG	1,4-BDO	DMPA
SPU	Organic solvent, without emulsifying	6	1	5	0
PWPU	Water, Pickering emulsion approach	6	1	5	0
SWPU	Water, self-emulsification	6	1	1.4	3.6

SWPU



the synthesis of self-emulsifyingwaterborne polyurethane(SWPU)

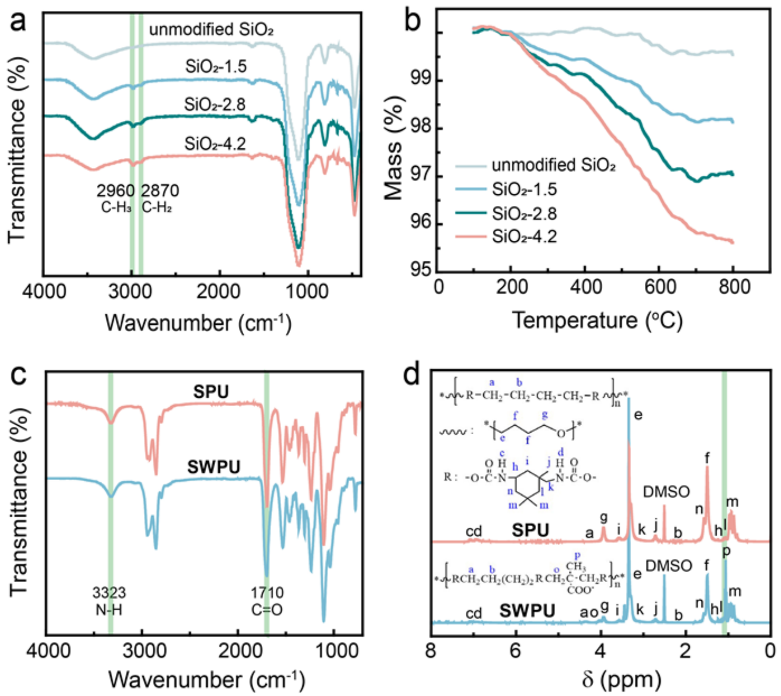
Surface modification of SiO_2 and its emulsifying property



Schematic illustration of SiO_2 modified by PTS

Table S1 The characterization data of modified SiO2 nanoparticles

Sample	Unmodified SiO_2/PTS/ water/ ethyl alcohol [a]	residual mass at 800°C (wt%)	mass loss at 800°C (wt%)	grafting rate (wt%)
UnmodifiedSiO_2	0	99.6	0	0
SiO_2-1.5	3/0.75/0.375/60	98.1	1.9	1.5
SiO_2-2.8	3/1.50/0.750/60	96.9	3.1	2.8
SiO_2-4.2	3/2.25/1.125/60	95.6	4.4	4.2



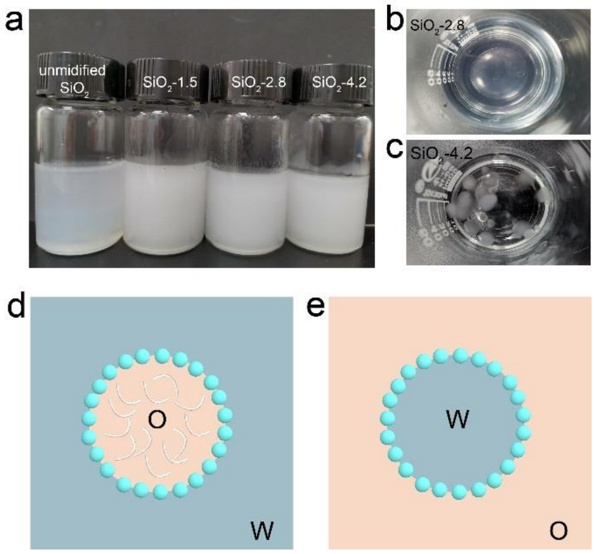


Figure 4(a) Photographs of Pickering emulsions stabilized by SiO_2-x particles**.** A drop of emulsions stabilized by **(b)** SiO_2-2.8;**(c)** SiO_2-4.2 particles dispersing in water. **(d)** oil-in-water (O/W) type emulsion; **(e)** water-in-oil (W/O) type emulsion.

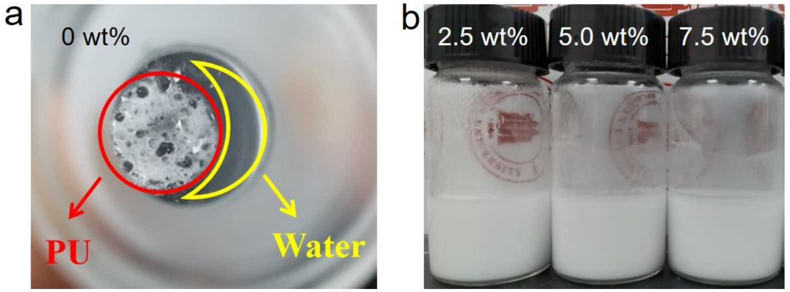
- Grafting rates of PTS on SiO_2 surface can be controlled by amount of PTS
- PTS grafting improve the emulsifying ability of SiO_2

- unmodified SiO_2 fails to stabilize emulsion

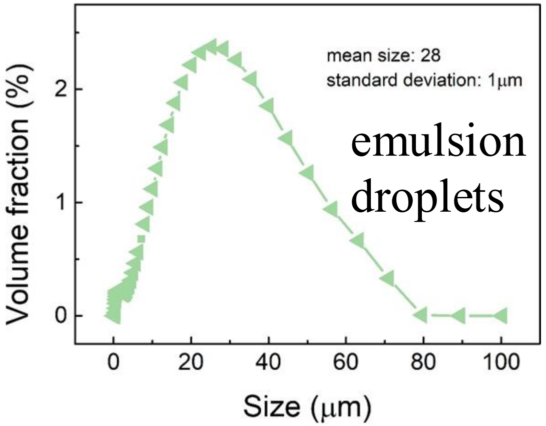
stable emulsions were obtained using modified SiO_2

- The emulsion stabilized by SiO_2-2.8 can remain dispersed in water (the oil-in-water type)
- The emulsion stabilized by SiO_2-4.2 is of water-in-oil type.

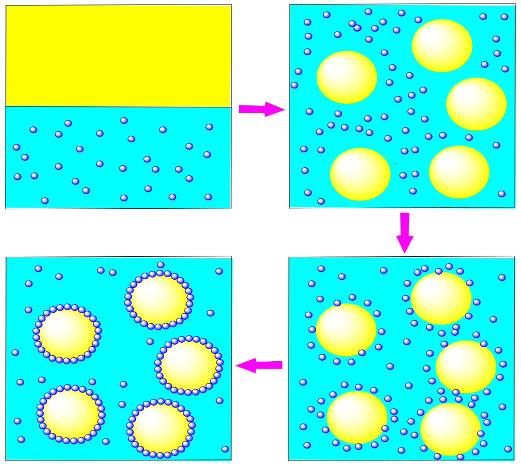
Emulsifying of polyurethane via Pickering emulsion approach

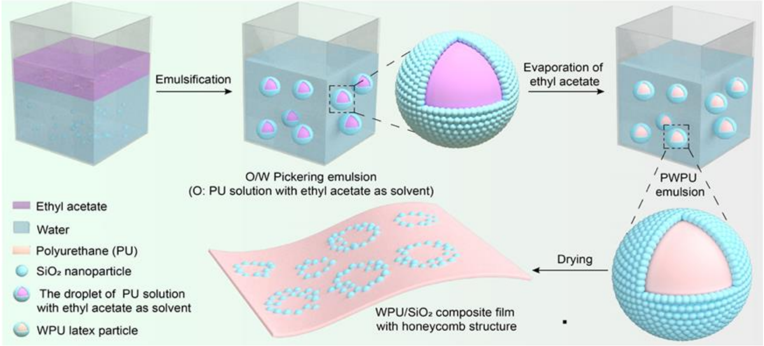


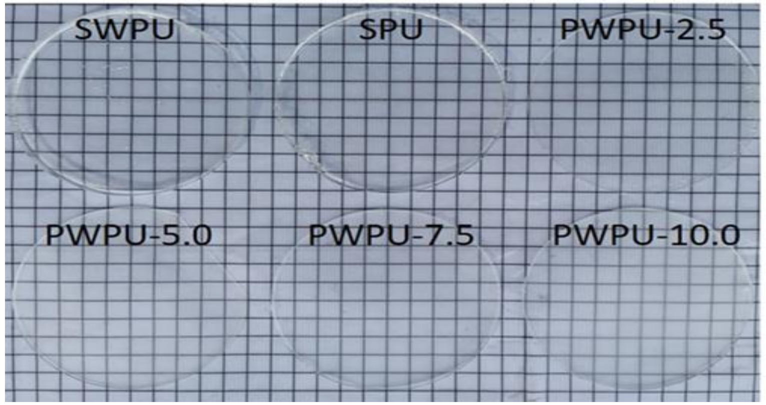
(a) Photographs of PWPUs **(a)** without SiO_2-2.8 and **(b)** with different SiO_2-2.8 concentrations.



Size distributions of the emulsion droplets in the Pickering







- The polyurethane fails to be dispersed in water in the absence of SiO_2-2.8,
- Stable emulsions can be formed when the dosage of SiO_2-2.8 exceeds 0.5 wt%
- The modified SiO_2 has proper wettability facilitating their adsorption at the oil-water interface to obtain stable Pickering emulsions
- all the PWPU composite films possess high transparency, implying the uniform dispersion of SiO_2 particles via Pickering emulsion approach

The wettability of particles and emulsion of PWPU

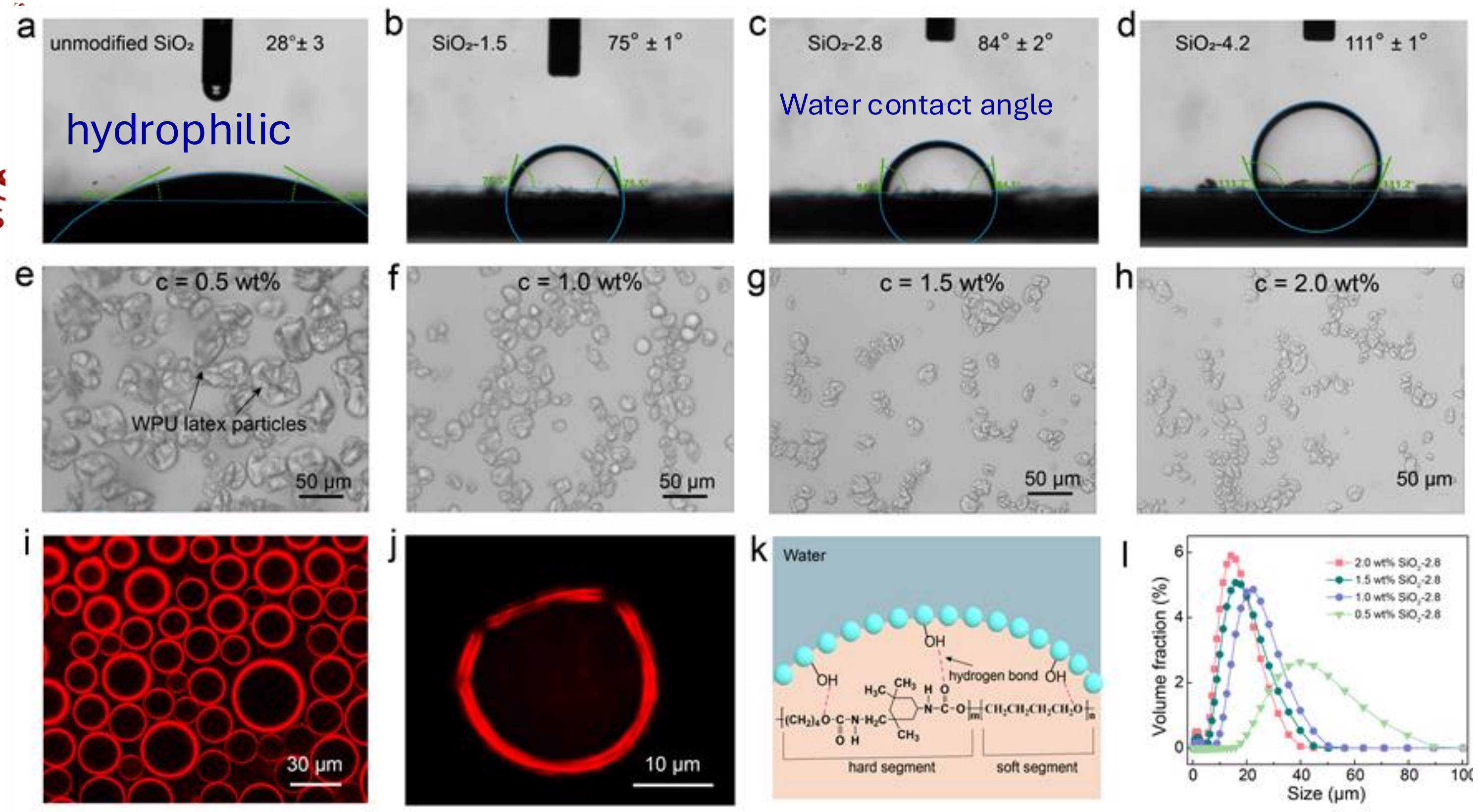


Figure 3 (a-d) WCA of unmodified SiO_2 nanoparticles and SiO_2-x nanoparticles in the ethyl acetate.
(e-h) Optical micrographs of PWPU dispersions stabilized by different SiO_2-2.8 concentration.
(i-j) CLSM images of Pickering emulsion with a PU dissolved in ethyl acetate as the oil phase, stabilized by 1 wt% rhodamine B-labeled SiO_2-2.8 nanoparticles.
(m) Schematic illustration of the hydrogen bond interactions between $_{SiO2\text{-}2.8}$ and polyurethane.
(n) size distributions of the WPU latex particles in PWPU dispersions stabilized by SiO_2-2.8

- PTS-grafting rate significantly affect the wettability of SiO_2 particles
- SiO_2-2.8 (WCA=75°) was selected as Pickering emulsifiers for PWPU (O/W type)
- SiO_2-4.2 exhibits a higher WCA (111°), facilitating the formation of a water-in-oil emulsion (W/O type)
- CLSM images clearly exhibit that almost all nanoparticles anchor on the PU/water interface
- PWPU dispersion maintains good stability after the removal of the oil solvent ethyl acetate)

Stability of PWPU dispersion

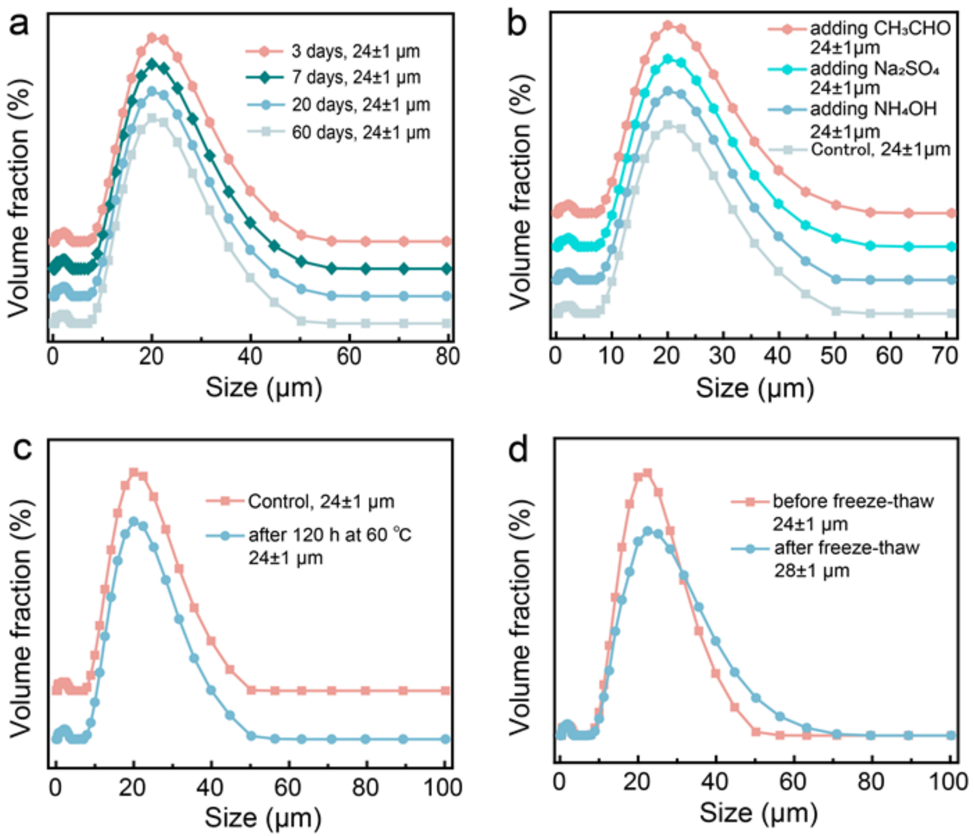


Figure 4 Mean size and distribution of the WPU latex particles in PWPU dispersion stabilized by 1.0 wt% SiO_2-2.8 after (a) storage for 3-60 days, (b) adding different chemicals, (c) heating for 120 h at 60 °C, and (d) three tests of freeze-thaw.

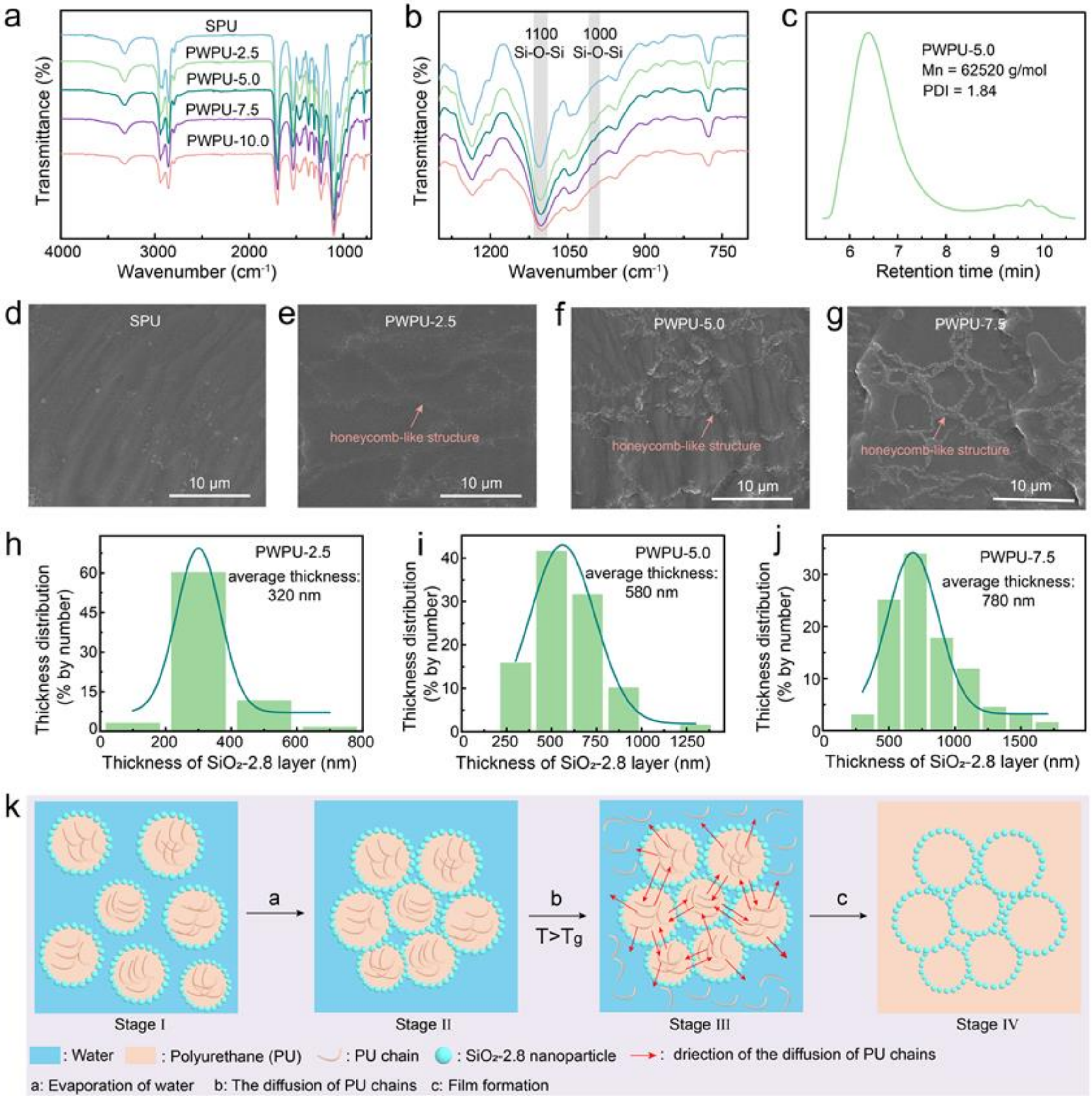
Table 3. Parameters of the PWPU dispersions prepared with different amounts of SiO_2-2.8

SiO_2-2.8 concentrations (wt%)	mean size of PWPU latex particles (μm)	size distribution of PWPU latex particles (μm)	solid content of PWPU dispersions	PWPU dispersions yield (%)
0	Unable to form PWPU emulsion			
0.5	45 ± 1	15~95	17.0 ± 0.5	73.7 ± 2.1
1.0	24 ± 1	4~50	22.6.0 ± 0.2	94.8 ± 1.0
1.5	19 ± 1	7~55	23.3 ± 0.4	96.5 ± 1.5
2.0	17 ± 1	4~50	24.1 ± 0.3	98.7 ± 1.2

- size of the WPU latex particles is 24 μm
- excellent long-term stability after storing for 60 days
- good chemical stability and thermal stability of PWPU dispersion meet the requirement of QB/T 2223-1996
- the good freeze-thaw stability

☐ the adsorption SiO_2 at the interface of PU and water is irreversible, acting as a physical barrier

Structures,morphologies and formation of PWPU films



- PWPU films resembled a striking honeycomb structure with thick wall.
- At higher content of SiO_2, larger thickness of the honeycomb wall is observed.
- This honeycomb structure is formed by SiO_2 that absorbed at the oil(PU)/water interface.

The presence of absorbed SiO_2 at WPU latex do not impede the film formation

Tg values of PWPU films (-75 ℃) is far below room temperature

- ☐ form heterogenous film at room temperature
- ☐ Good film-forming ability

Figure 5 FT-IR spectra of SPU and PWPU films ranging from **(a)** 4000 to 700 cm^{-1} and **(b)** 1300 to 700 cm^{-1}. **(c)** GPC trace of PWPU-5.0. **(d-g)** The SEM images of cross-sectional morphologies of SPU and PWPU films. **(h-j)** Thickness distributions of honeycomb walls in PWPU films. **(k)** Schematic illustration of film formation process of PWPU dispersion.

Mechanical properties, water resistance of PWPU films

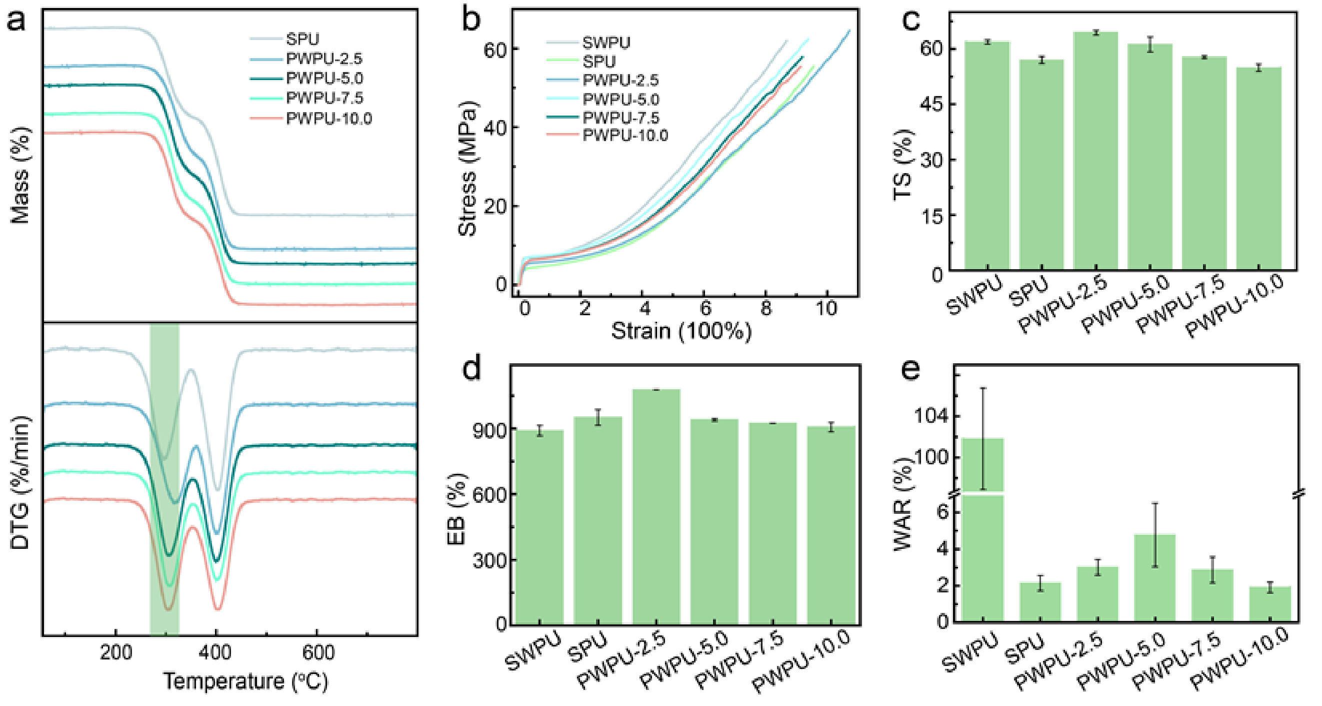


Figure 6 (a) TGA and DTG curves, (b) stress-strain curves, (c) tensile strength, (d) elongation at break, and (e) water absorption rate of films.

- PWPU films exhibit better mechanical properties as reflected by the higher TS and EB values
- confirming the reinforcement of SiO_2

- thermal stability of PWPU are comparable or even higher than those of solvent PU (SPU) and self-emulsifying waterborne polyurethane (SWPU) films.

- PWPU films show very low water absorption rate (≤6%), as low as that of solvent PU film.
- Self-emulsifying SWPU film has the highest WAR (101.8%)
- the enhanced water-resistance of the cured film via Pickering emulsion approach

Leather coating application of PWPU composite film

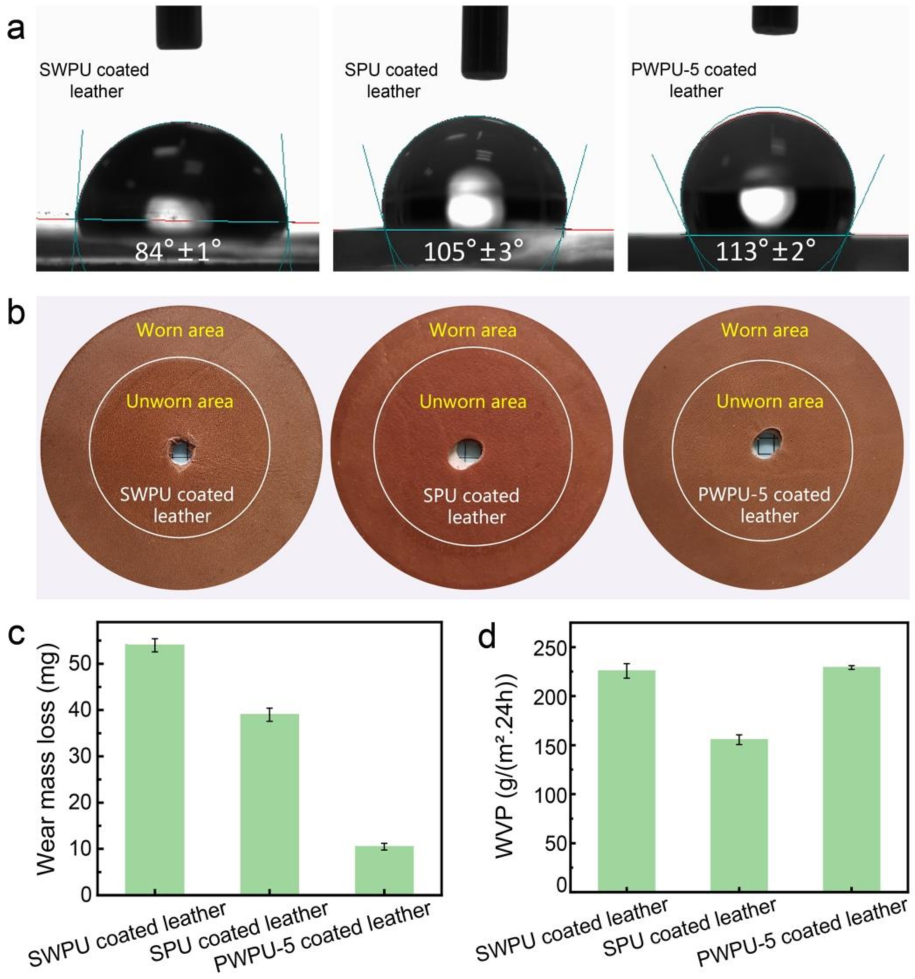


Figure 7 **(a)** water contact angles, **(b)** appearance (before and after abrasion test), **(c)** wear mass loss, **(d)** water vapor permeability of SWPU, SPU, and PWPU-5 coated leather.

- PWPU-5 was selected for leather finishing
- WCA of PWPU coated-leather is even higher than SPU
- PWPU coated-leather have slight change in brightness and no wear marks is observed; the wear mass loss is the lowest (10.5mg).
- water vapor permeability (WVP) of PWPU coated leather is as high as that of SWPU-coated leather.

Advantages of PWPU coated Leather:

- Better abradability
- Better surface hydrophobicity
- Good Hygiene performance comparable to SWPU coated leather

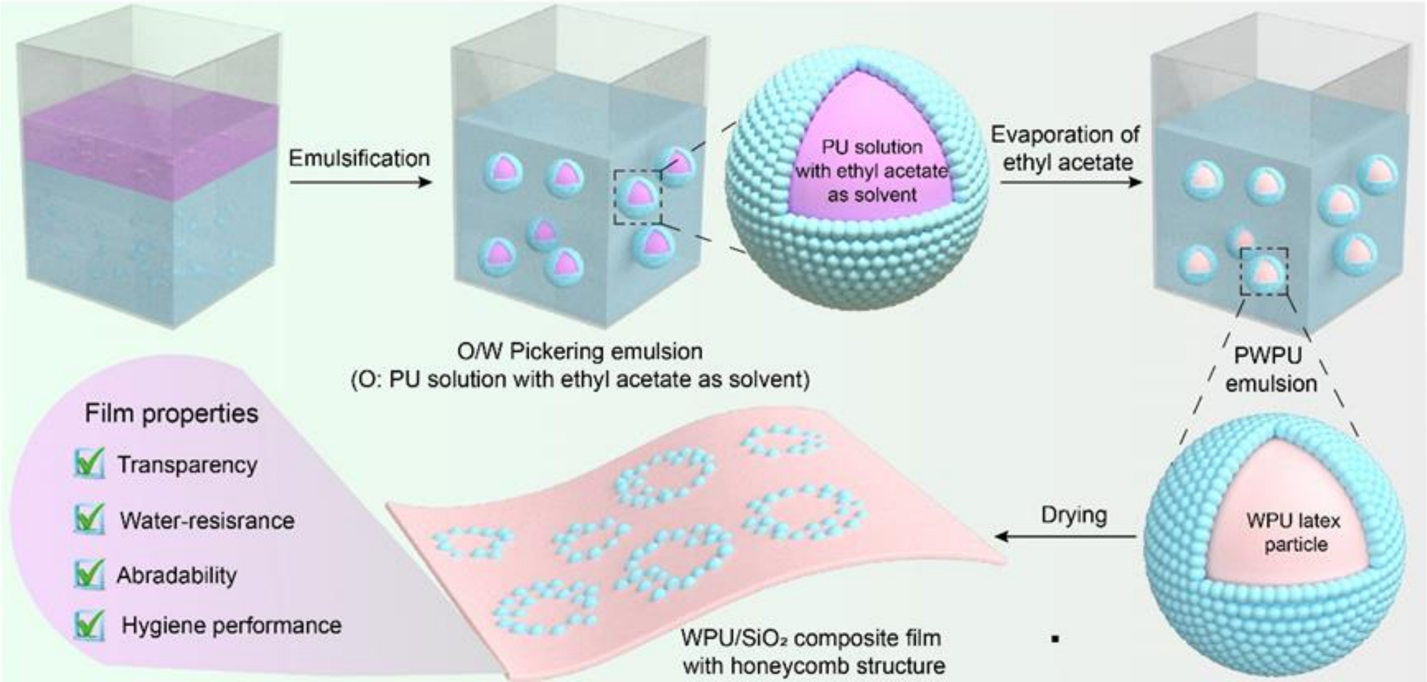
Summary

First study on the preparation of WPU via Pickering Emulsifying Approach.

The water-resistance of PWPU is comparable to that of solvent PU.

PWPU-coated leather shows better abrasion resistance and hygiene performance

This work demonstrates that Pickering emulsion approach can be used as a potential strategy to fabricate waterborne polyurethane emulsions for film application such as leather finishing.



The role of SiO_2 in PWPU by Pickering approach

- ☐ Act as stabilizer in PWPU emulsions (achieving the dispersion of PU in water)
- ☐ reinforcement effect on PWPU film
- ☐ Improve abrasion resistance
- ☐ Enhance water-resistance (solvent PU)
- ☐ Environment friendly (> solvent PU)

COLLAGEN and LEATHER

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Scope

Fundamental researches of collagen
Novel utilization of collagen
Tanning chemistry
Leather chemicals
Novel technology of leather manufacture
Polymeric materials and coating technology
Cleaner production and environmental management
Collagen biomaterials
Collagen functional materials
Collagen utilization in food industry
Transdisciplinary researches related with collagen and leather
Biomass conversion and renewable materials

- **Open Access**
- **APC Free**
- **ESCI, EI, Scopus**
- **IF 9.2, CiteScore 10.2**
- **Chemistry, Applied (7th, top 9%); Materials Science, Multidisciplinary (66th, top 14%)** **Q1**

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The Pickering waterborne polyurethane emulsion (PWPU) was successfully fabricated by using SiO_2 nanoparticles as Pickering stabilizer. The good Pickering emulsion effects can be achieved by the optimized hydrophobic modification of SiO_2, as verified by the excellent emulsion stability of PWPU. The PWPU films present high transparency and morphology of honeycomb structures, revealing that the Pickering stabilizer would not hinder the film formation process of PWPU if cured at room temperature. The film performance of PWPU particularly the mechanical property and thermal stability are comparable or even higher than those of the solvent-based polyurethane and self-emulsifying waterborne polyurethane (SWPU) films. It is noted that the water uptake of the PWPU film is approximately 20 times lower than that of SWPU, demonstrating that the introduction of SiO_2 nanoparticles via Pickering emulsion approach contributes to the enhancement of water-resistance of WPU films significantly. More importantly, the leather coated with PWPU exhibits better hydrophobicity, abrasion resistance and water vapor permeability than either SPU or SWPU coated-leather. This work demonstrates that Pickering emulsion approach can be used as a potential strategy to fabricate waterborne polyurethane emulsions for film application such as leather finishing.

Table S3. Parameters of the PWPU dispersions prepared with different amounts of SiO_2-2.8

SiO_2-2.8 concentrations (wt%)	mean size of PWPU latex particles (μm)	size distribution of PWPU latex particles (μm)	solid content of PWPU dispersions	PWPU dispersions yield (%)
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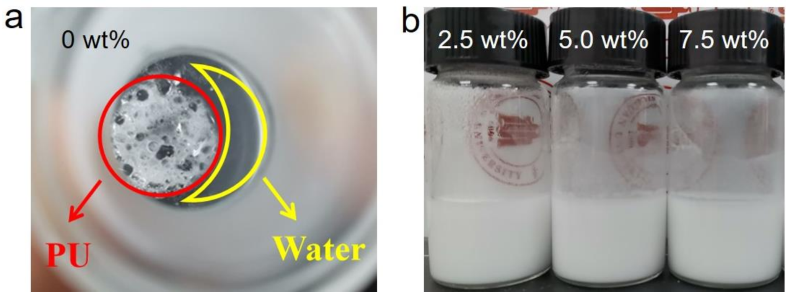
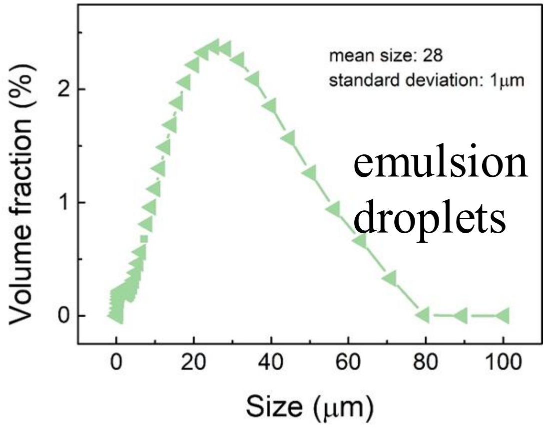
1.5	19 ± 1	7~55	23.3 ± 0.4	96.5 ± 1.5
2.0	17 ± 1	4~50	24.1 ± 0.3	98.7 ± 1.2

- The conversion rate of the PWPU dispersions is above 94% when the content of SiO2-2.8 exceeds 1.0 wt% (Table S3)
- PWPU dispersion with high conversion rate can be obtained via Pickering emulsion approach

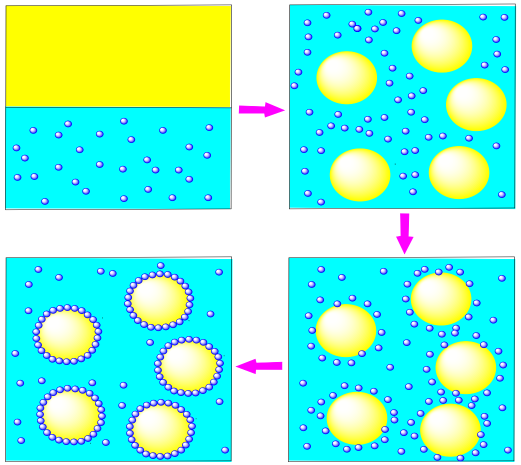
Emulsifying of polyurethane via Pickering emulsion approach



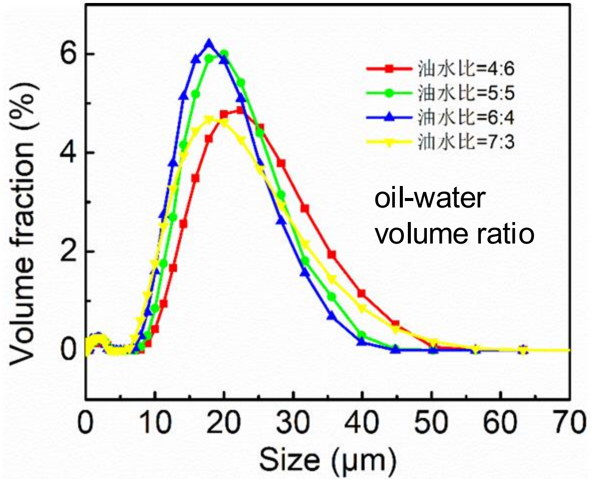
(a) Photographs of PWPUs **(a)** without SiO_2-2.8 and **(b)** with different SiO_2-2.8 concentrations.



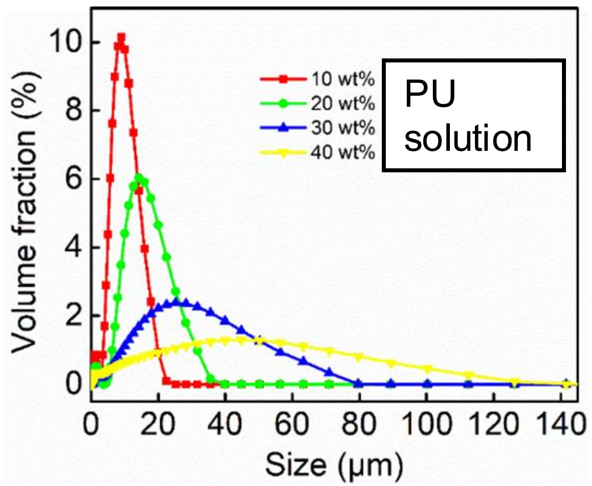
Size distributions of the emulsion droplets in the Pickering



Effect of oil-water volume ratio



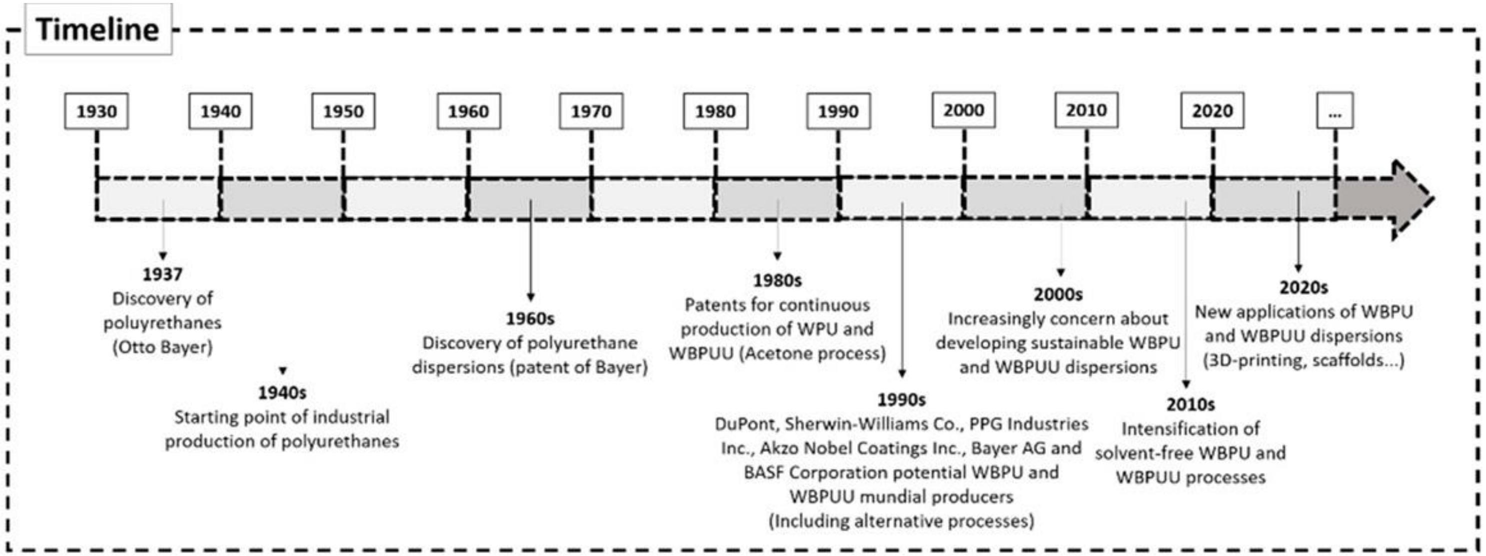
PU concentration



unmodified SiO_2 fails to stabilize the emulsion
stable emulsions were obtained by using modified SiO_2

When the oil-water volume ratio at 6:4，the size of emulsion droplets

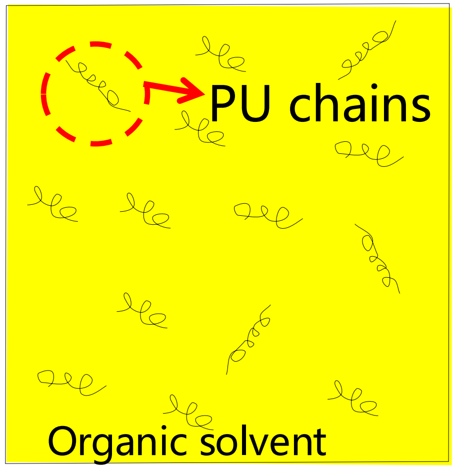
油水比为6: 4时，乳液粒径最小



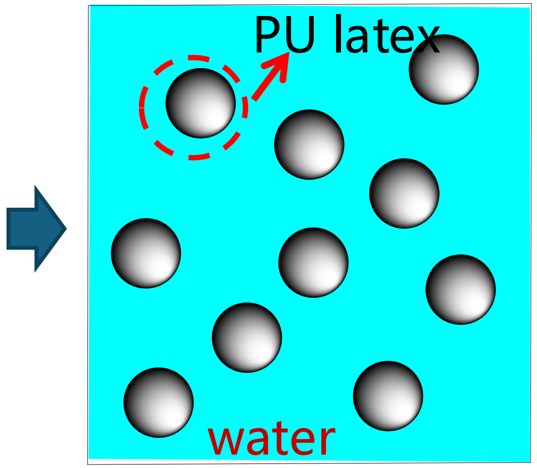
Timeline
1930
1940
1950
1960
1970
1980
1990
2000
2010
2020
...
1937
Discovery of poluyrethanes (Otto Bayer)
1940s
Starting point of industrial production of polyurethanes
1960s
Discovery of polyurethane dispersions (patent of Bayer)
1980s
Patents for continuous production of WPU and WBPUU (Acetone process)
1990s
DuPont, Sherwin-Williams Co., PPG Industries Inc., Akzo Nobel Coatings Inc., Bayer AG and BASF Corporation potential WBPU and WBPUU mundial producers (Including alternative processes)
2000s
Increasingly concern about developing sustainable WBPU and WBPUU dispersions
2010s
Intensification of solvent-free WBPU and WBPUU processes
2020s
New applications of WBPU and WBPUU dispersions (3D-printing, scaffolds...)

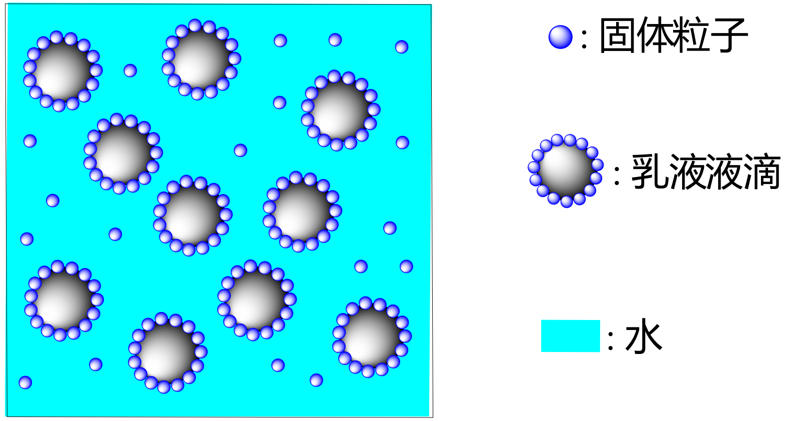
Background

Solvent PU



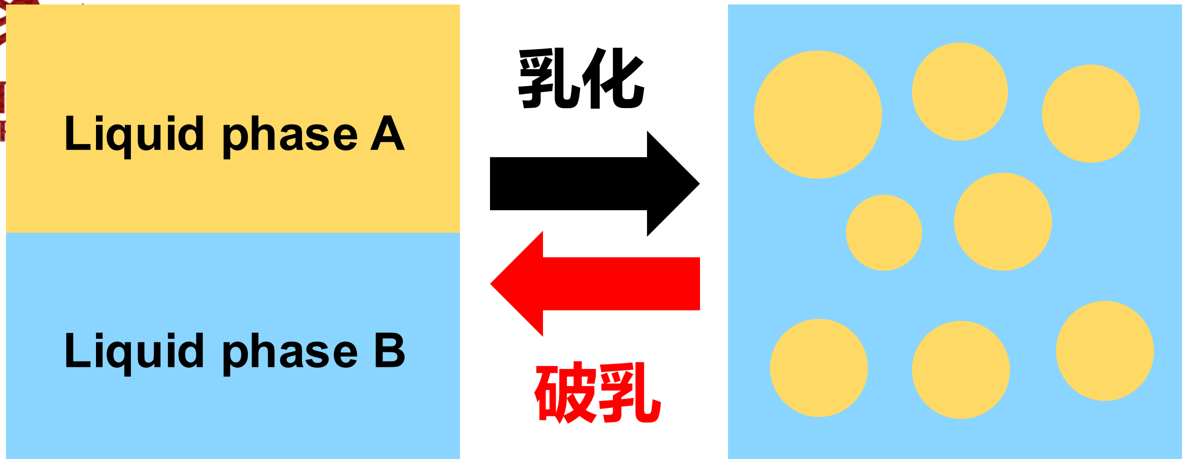
WPU (environmental -friendly)





1.1 Pickering乳液

(a)



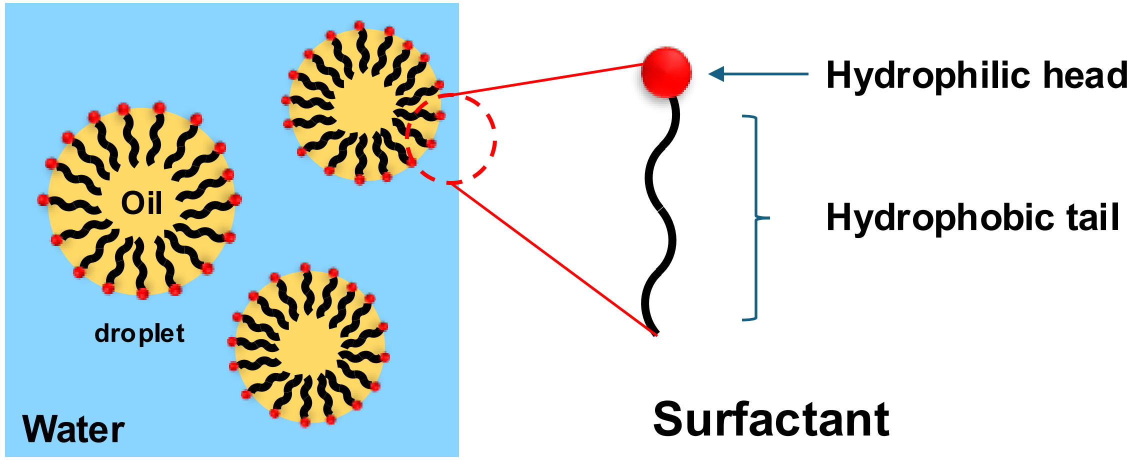
(b)

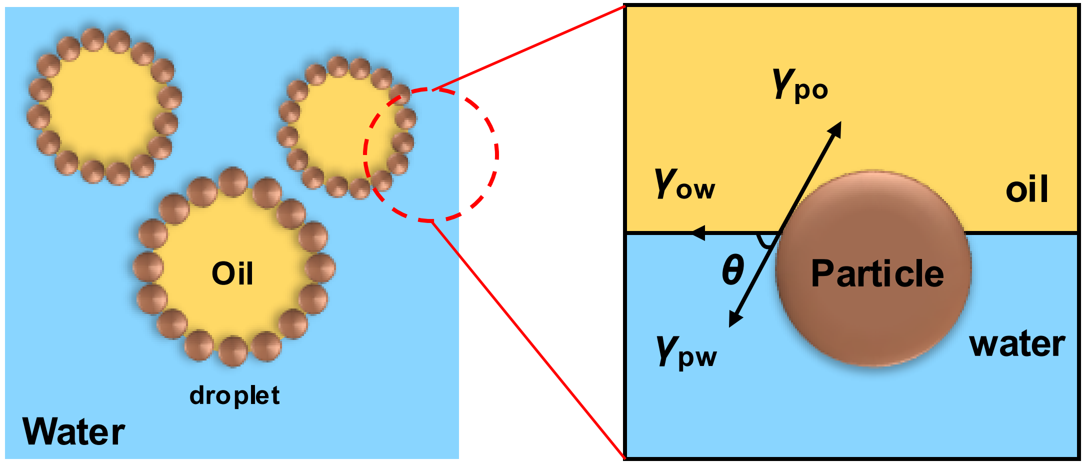
➢ **乳化过程的能量变化**

$$\Delta H = \gamma \Delta A \quad (1\text{-}1)$$

$$\Delta G = \Delta H - T\Delta S \quad (1\text{-}2)$$

- $\Delta G > 0$，乳液是热力学不稳定体系





- 表面活性剂稳定乳液[1]
- Pickering乳液：固体颗粒稳定的乳液[2]

[1] Nakama Y. *Cosmetic Science and Technology*, 2017: 231-244. [2] Pickering S U. *Journal of the Chemical Society*, 1907, 91(0): 2001-2021.