CRYSTAL MORPHOLOGY

CRYSTAL MORPHOLOGY

Crystallinity

the crystallization of a wax is counterproductive to the gloss of an oleogel, which is dependent on the refractive index

waxes with high crystallinity (large crystals) usually reduce the glossiness of a formulation

due to their crystallinity waxes do not form transparent systems

high crystalline **less gloss**	**low crystalline** **more gloss**
Beeswax white	Sunflower Seed Wax
Rice Bran Wax	Carnauba Wax
Berry Wax	Candelilla Wax
Myrica Fruit Wax	Shellac Wax
Jasmine Wax	
Rapeseed Wax	

CRYSTAL MORPHOLOGY

Crystallization behavior

- the critical oleogelling concentrations of a wax are attributed to the polarity of the used emollients
- the gelling behavior can be tuned by altering the cooling time / temperature and shear rates
- crystal morphology significantly changes depending on the type of oil used
- the quality and purity of a wax also significantly impacts the crystal morphology, which directly affects the oil-structuring property of that wax
- the rheological and thermal properties of an oleogel are driven by the crystallization behavior of the wax

CRYSTAL MORPHOLOGY

Oleogelling

CP (cone penetration) @RT (25 °C), 20% of wax	properties	in castor oil (polar)	in octyldodecanol (medium polar)	in paraffinum perliquidum (nonpolar)
Carnauba Wax	most polar natural wax	31	79	37
Candelilla Wax	100 % wax	37	84	48
Beeswax white	100 % wax	40	152	96
Rice Bran Wax	100 % wax	31	55	82
Sunflower Seed Wax	most nonpolar natural wax	31	51	49

the lower the CP the harder is the tested material

depending on their polarity and chemical composition, waxes create with different emollients a varying oleogel hardness

CRYSTAL MORPHOLOGY

Crystallization and re-crystallization

- theoretically wax crystals do not grow over time
- only butters, hydrogenated oils, fats and waxes, which are chemically triglycerides, change their crystal size over time
- in unfavorable combinations this can cause visible crystals on the surface of cosmetic products over time (so-called blooming)
- low quality waxes with a high number of impurities can trigger blooming as matrix for crystallization

CRYSTAL MORPHOLOGY

Influence of production conditions

waxes need to be heated approx. 20 °C over their melting point to ensure all crystals are entirely molten and particles can move freely

fast melting and melting at high temperatures increase hardness/viscosity

long heating time and repeated melting reduce hardness/viscosity

filling behavior and temperature of oleogels have a crucial impact on final hardness/stability

simple oil-wax blends poured at 35 °C are usually instable semiliquids, but poured at 80 °C form stable, homogenous oleogels

variations in production procedure lead to different results

oleogels from production are usually softer due to the longer manufacturing times

CRYSTAL MORPHOLOGY

Influence of production conditions

if bulk completely congeals, re-heating over cloud point is necessary to break structure again

when hot wax cools, the cloud point refers to the temperature at which the transparent melt changes to a cloudy semiliquid due to the growing crystal matrix

agitation of oleogels below the cloud point destroys the crystalline structure

re-heating of bulks (especially polyethylene-based ones) that have been stirred almost until congealed show a lower hardness but are much creamier and have a better heat resistance; additionally, entrapped air bubbles get released

CRYSTAL MORPHOLOGY

Influence of production conditions

fast cooling results in smaller crystals and harder oleogels, but can cause extreme shrinkage and cracks

cooling effect is faster in the outer zone especially in metal molds; therefore, a discrepancy can occur between outer and inner zone that endangers stability (breakage)

slow cooling at room temperature often results in the most stable formulations, but is not practiced as a lot of space and time would be necessary

CRYSTAL MORPHOLOGY

Formulating and up-scaling issues

the crystallinity, melting and congealing behavior change significantly when the pure wax is combined with oils

depending on the oils, the DSC curve differs from the one of pure wax

it is unpredictable if the formulation is not fully known

even when the formulation is known there are many interactions between waxes and oils which can lead to unexpected results

CRYSTAL MORPHOLOGY

Troubleshooting – blooming effect

- occurs the fastest at storage temperatures of 12–18 °C some weeks/months after filling
- if it appears earlier, it is probably an incompatibility of raw materials or caused by mold release agent
- low melting butters, waxes, and triglycerides can induce blooming
- the crystal growth is further triggered by pigments
- small α-crystals over time form larger β- and γ-crystals that become visible on the surface

Troubleshooting – blooming effect

the problematic ingredients should be reduced or replaced

the addition of some emulsifiers helps against blooming, as they reduce surface tension and therefore have an impact on crystal formation

- 2 % Sorbitan Esters/Stearates (e.g., 45 % GMS or glycerol monolaurate)
- 0.2–0.7 % Lecithin

the addition of bentonite can also help as it forms an additional stabilizing network

CRYSTAL MORPHOLOGY

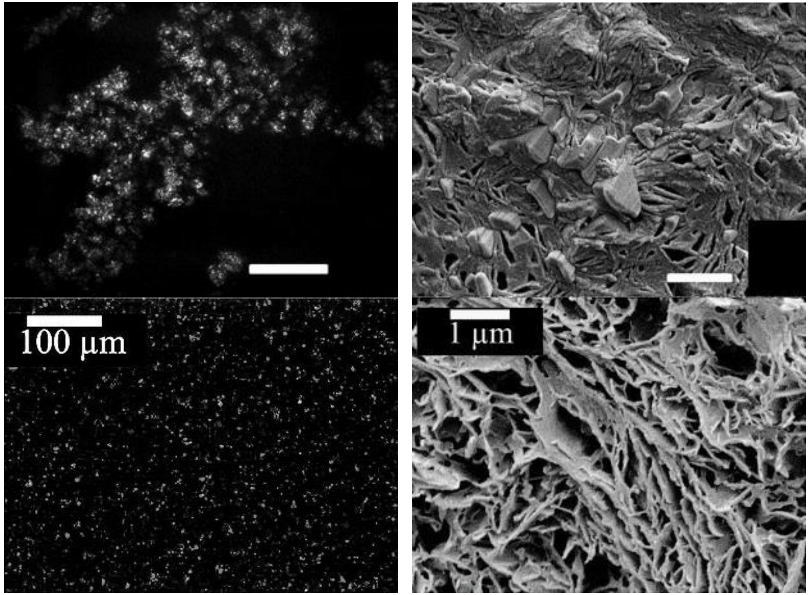
Microscopy

there are two methods of microscopy that are used to visualize crystal morphology:

- PLM (polarized light microscopy)
- CRYO-SEM (cryo-scanning electron microscopy)

one of the decisive differences is that PLM makes recognizable if there is co-existence or co-crystallization of crystals

PLM CRYO-SEM



Crystallization behavior – candelilla wax

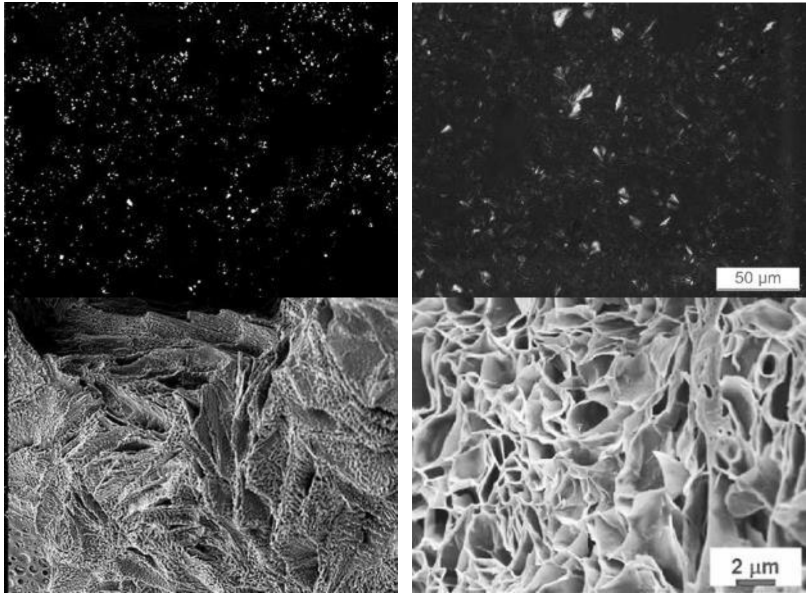
solvent polarity has a very important impact on gelation behavior of natural waxes

candelilla wax crystallizes into very fine linear or grain-like particles that are further organized into an open aggregate-like structures with sparse packing, probably due to a high proportion of linear hydrocarbons

the high oil binding capacity is attributed to the small particle size in the gel, the high surface area, as well as the homogeneous distribution throughout the material

in rice bran oil a more needle-like crystal morphology was observed

in high oleic sunflower oil | in rice bran oil



pictures were obtained via polarized light microscopy and cryo-SEM

CRYSTAL MORPHOLOGY

Crystallization behavior – beeswax

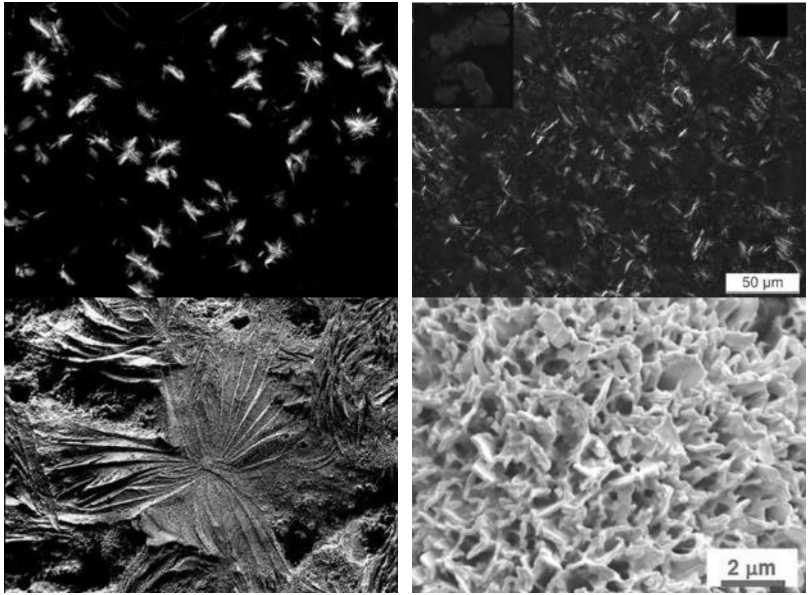
solvent polarity has a very important impact on gelation behavior of natural waxes

beeswax crystals showed varying morphologies – big spherulite crystals (in canola, soybean, and sunflower oil) and needle-like crystals (in corn, olive, and safflower oil)

in sunflower oil the spherical-type crystals prevail, which connect into a network by weak yet uniform type of bonding

in rice bran oil both kinds of crystal morphologies are present and interact very well leading to a close network and strong gelling property

in high oleic sunflower oil   in rice bran oil



pictures were obtained via polarized light microscopy and cryo-SEM

CRYSTAL MORPHOLOGY

Crystallization behavior – carnauba wax

solvent polarity has a very important impact on gelation behavior of natural waxes

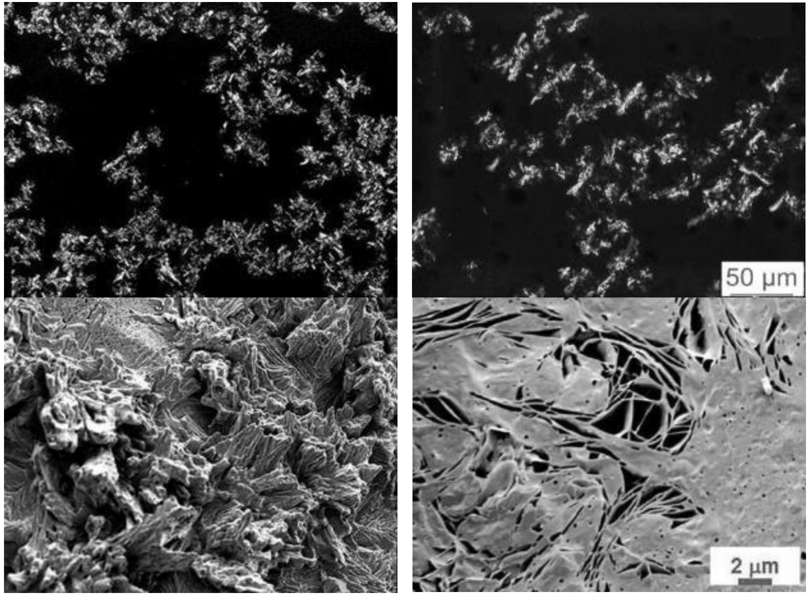
in sunflower oil: carnauba wax forms three-dimensional crystals (<10 µm) which are stacked closely together into larger aggregates (50–100 µm)

network formation due to the overlapping of spherical volumes of these aggregates

the observed strong shear thinning behavior is attributed to the disruption of aggregate clusters into smaller ones

in canola oil/rice bran oil: carnauba wax forms dendritic crystals (50–100 µm), not ideal for binding oil, resulting in a weak network

in high oleic sunflower oil | in rice bran oil



pictures were obtained via polarized light microscopy and cryo-SEM

CRYSTAL MORPHOLOGY

Crystallization behavior – rice bran wax

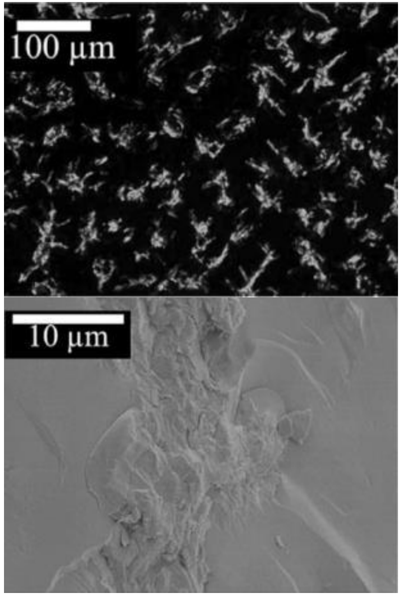
solvent polarity has a very important impact on gelation behavior of natural waxes

in rice bran oil (similar in liquid paraffin) rice bran wax forms long dendritic crystals, which interconnect to form a branched network with many voids resulting in weak gelling ability and low oil binding capacity

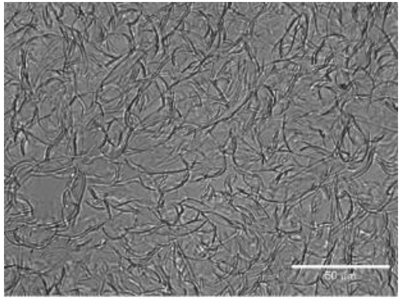
those dendritic molecules that interfere with the network development are formed by the minor free fatty acid fraction in rice bran wax

in olive oil & canola/soybean oil rice bran wax crystals have thin long needle-like shape, which positively contribute to gelation

in rice bran oil



in canola oil



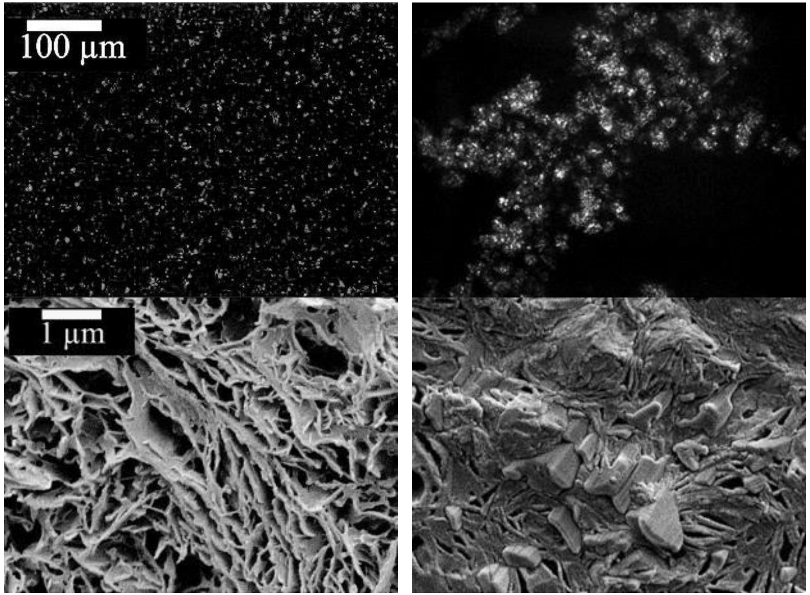
pictures were obtained via light microscopy and cryo-SEM

Crystallization behavior – berry wax

- solvent polarity has a very important impact on gelation behavior of natural waxes
- berry wax's needle-like crystals can reinforce network structures of high melting waxes (e.g., rice, sunflower, candelilla wax) by forming solid crystal bridges between the pre-existing crystals (called "sintering") – ideal for enhancing structures of other crystallizing materials
- it displays a slow crystallization and lateral packing, so viscosity and stability can increase with storage time
- in high oleic sunflower oil and without other waxes, berry wax shows platelet-like crystals in spherical aggregates, which form a rather weak but elastic network

in rice bran oil

in high oleic sunflower oil



pictures were obtained via polarized light microscopy and cryo-SEM

CRYSTAL MORPHOLOGY

Crystallization behavior – myrica fruit wax

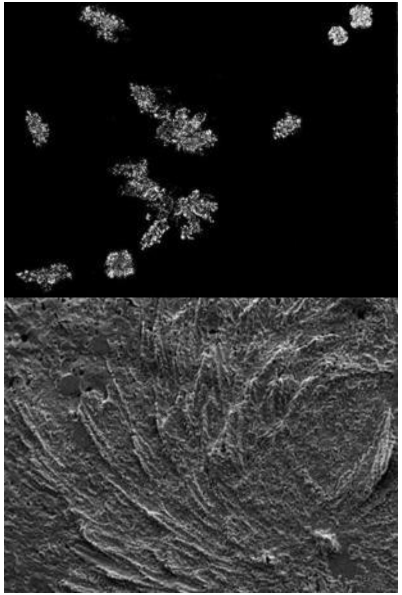
solvent polarity has a very important impact on gelation behavior of natural waxes

myrica wax forms flat crystals that are seen radiating outward from the center to form spherical units (30–50 μm)

these spherulite crystals are not favorable for entrapping liquid oil, causing weak conjunctions and unstable gels → low gelling capacity

the elasticity of myrica wax oleogels is attributed to loose entanglements of large crystals but because of this structure, the gels can only sustain lower magnitude of stress

in high oleic sunflower oil



pictures were obtained via polarized light microscopy and cryo-SEM

Crystallization behavior – sunflower seed wax

solvent polarity has a very important impact on gelation behavior of natural waxes

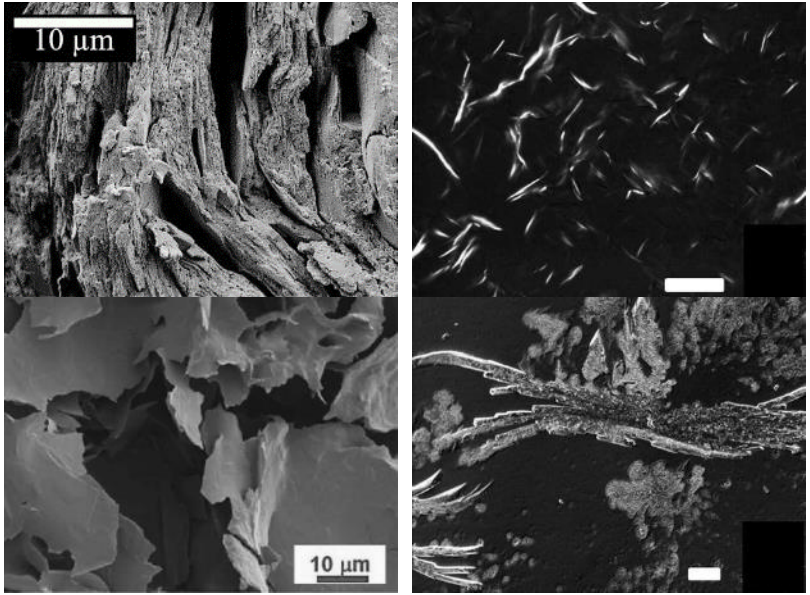
sunflower wax has the tendency to form thin plate-like crystals, piled upon each other (observed in different liquid oils such as sunflower oil, soybean oil, and rice bran oil)

sunflower wax shows a high gelling capacity, which is attributed to its long chain wax esters

its needle-like morphology leads to the formation of good crystalline matrices that make up a dense and strong network

in rice bran oil

in high oleic sunflower oil



pictures were obtained via light microscopy and cryo-SEM

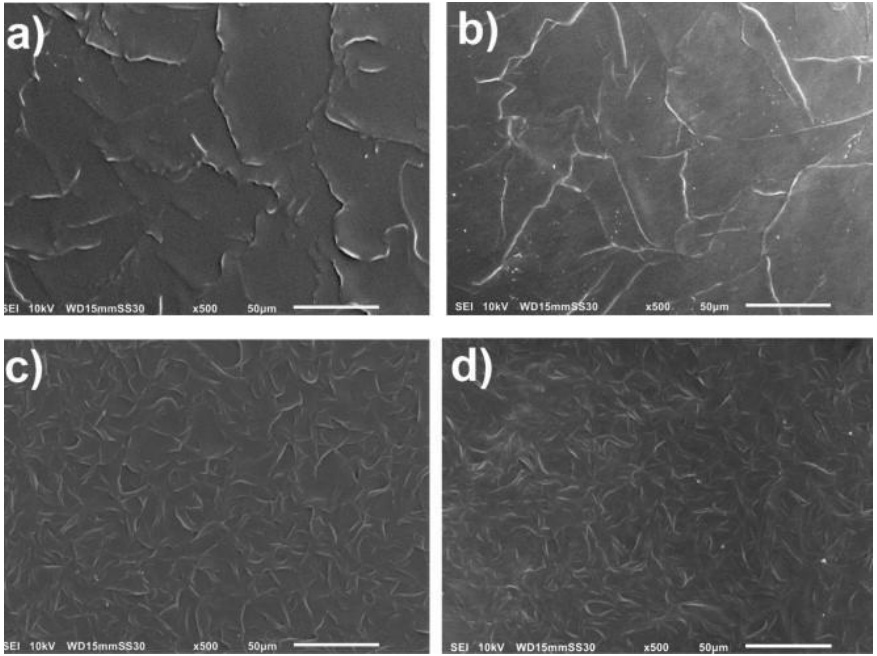
CRYSTAL MORPHOLOGY

Sunflower seed wax in soybean oil

PLM of 5 % Sunflower Seed Wax in soybean oil oleogel at different resolutions

the platelet-like crystals are well connected to each other to form dense networks

the strong oil-binding ability can be explained by the effectiveness of immobilization of oil with the networks of numerous thin platelet-like crystals

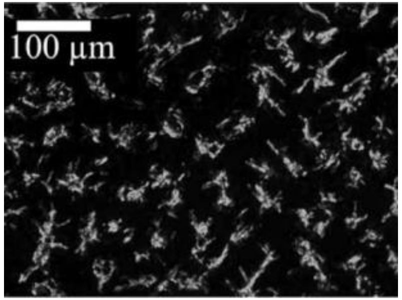


a), b), c), d) represent different resolutions

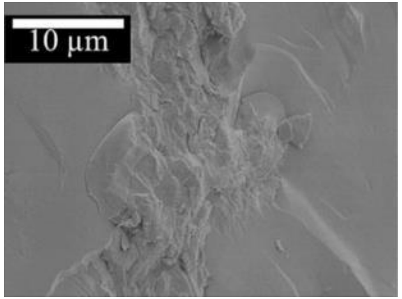
Wax synergies of rice bran wax

- oleogel with 5 % Rice Bran Wax in rice bran oil
- rice bran wax forms loose crystals and no solid networks
- combined with sunflower seed wax their crystals only co-exist and do not co-crystallize, forming no mixed crystals
- low-melting berry wax can reinforce the network by crystallizing in the voids remaining after crystallization of the high-melting wax
- additionally, solid bridges between the crystals of berry wax and rice bran wax (sintering) further strengthened the network structure

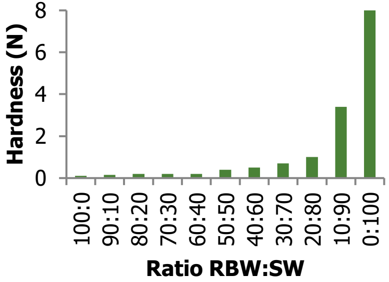
PLM

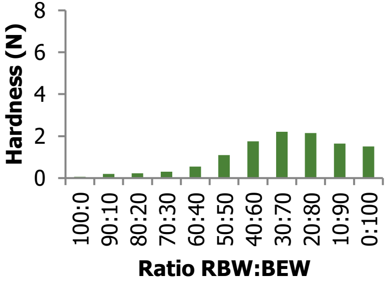


CRYO-SEM



Hardness of oleogels in combination with other waxes





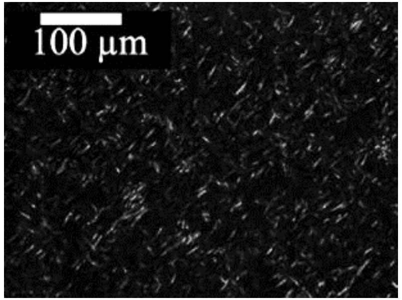
RBW= Rice bran wax; SW= Sunflower seed wax; BEW= Berry wax

CRYSTAL MORPHOLOGY

Wax synergies of sunflower seed wax

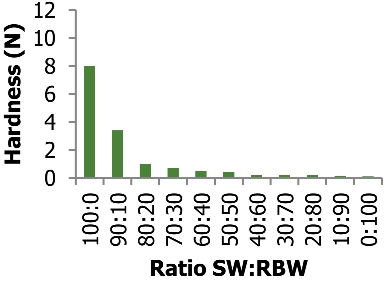
- oleogel with 5 % Sunflower Seed Wax in rice bran oil
- sunflower seed wax forms solid platelet-like crystals networks
- combined with rice bran wax, both waxes crystallize simultaneously, resulting in only co-existing crystals which do not mix
- low-melting berry wax can reinforce the network by crystallizing in the voids remaining after crystallization of the high-melting wax
- additionally, solid bridges between the crystals of berry wax and sunflower seed wax (sintering) further strengthened the network structure

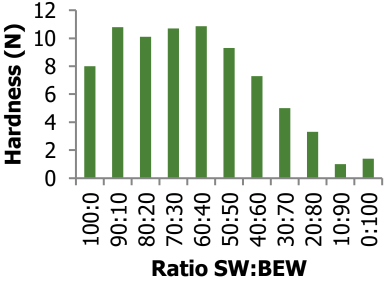
PLM



CRYO-SEM

Hardness of oleogels in combination with other waxes



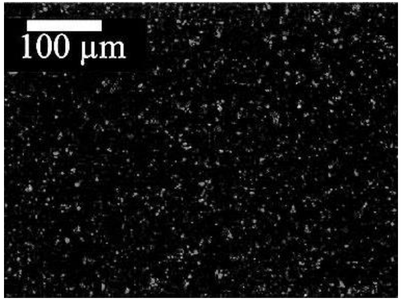


RBW= Rice bran wax; SW= Sunflower seed wax; BEW= Berry wax

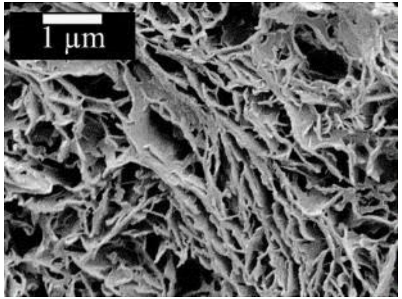
Wax synergies of berry wax

- oleogel with 5 % Berry Wax in rice bran oil
- berry wax crystals appear to be needle-like forming bridges between existing crystals
- the phenomenon is called sintering and creates very stable but flexible structures with an excellent oil binding capacity
- sintering of berry wax is a form of co-crystallization (cohesive network) that occurs with all commonly used natural waxes

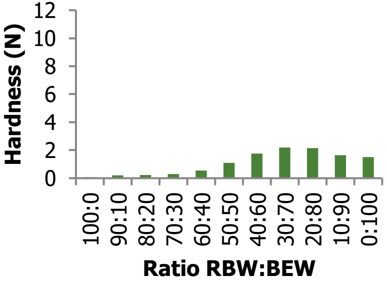
PLM

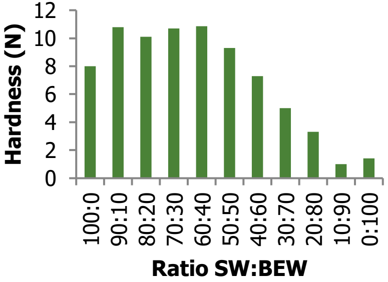


CRYO-SEM



Hardness of oleogels in combination with other waxes





RBW= Rice bran wax; SW= Sunflower seed wax; BEW= Berry wax

CRYSTAL MORPHOLOGY

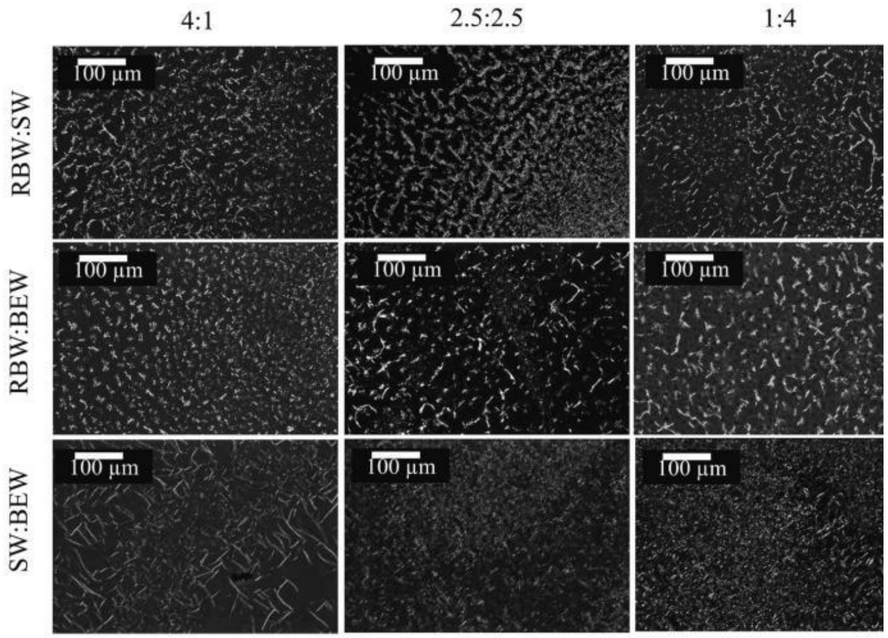
Wax synergies at different ratios

PLM images of rice bran oil oleogels with Rice Bran Wax (RBW), Sunflower Seed Wax (SW) and Berry wax (BEW) at different ratios

rice bran and sunflower wax crystallize simultaneously, resulting in co-existing crystals which do not mix

only a small amount of BEW was required to introduce sintering in the SW network, because SW already forms a dense crystal network → best interaction at 1% BEW:4% SW

in combination with RBW, a higher amount of BEW is required, because RBW only forms a loose crystal network structure → best interaction at 4% BEW:1% RBW

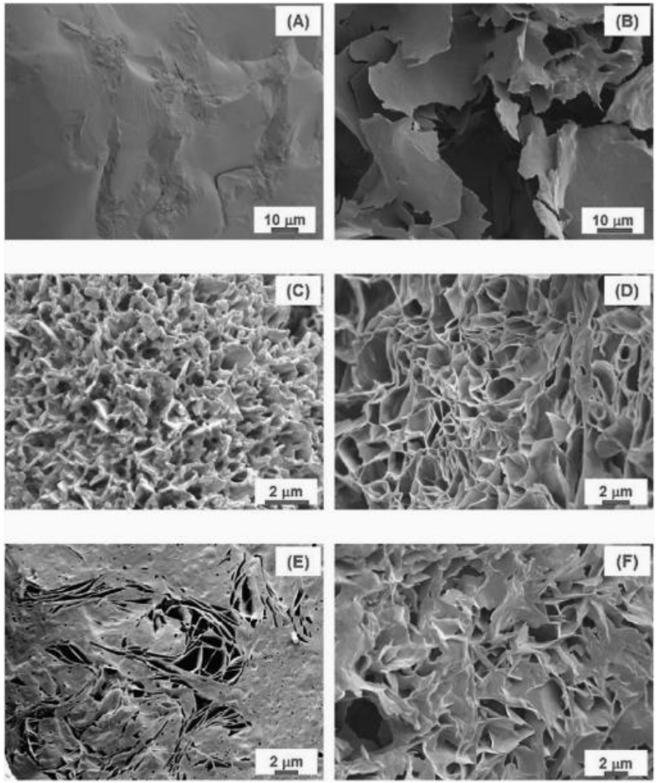


Cryo-SEM of different waxes

CRYO-SEM of rice bran oil oleogels with 5 %

A) Rice Bran wax:	long dendritic crystals
B) Sunflower Seed wax:	platelet crystals
C) Beeswax:	needle-like crystals
D) Candelilla wax:	needle-like crystals
E) Carnauba wax:	large dendritic crystals
F) Berry wax:	needle-like crystals

but the morphology is dependent on the used oil and can vary!



Thank you!