coatings

Supplementary Materials

1. Critical Micelle Concentration (CMC)

So far, no clear emulsifier concentrations have been published in the literature for use in candelilla wax emulsions. However, in a previous publication [42] it was shown, that for a carnauba wax (which is chemically similar to candelilla wax)-based emulsion, an increase from 0.3% to 1% emulsifier reduced the particle size by about 30%. Thus, at this low concentration, the availability of the emulsifying molecules had a strong effect, and the critical micelle concentration (CMC) was not yet reached. Based on the values of this publication, we draw up a simple geometrical model to estimate how much the particle size could further change, when introducing more emulsifier. For this, we made some assumptions:

- The volume of wax stays constant, before (Index 1) and after emulsification (Index 2).
- The specific surface (S) and amount of particles (n) increases, due to emulsification.
- The specific surface (S) that can be covered with an emulsifier E, linearly correlates with the emulsifier concentration $c(E)$.

This leads to the following geometrical mathematical correlations:

$$V_1 = V_2$$

$$n_1 \times \frac{4}{3} \times \pi \times r_1^3 = n_2 \times \frac{4}{3} \times \pi \times r_2^3$$

$$n_2 = n_1 \times \frac{r_1^3}{r_2^3}$$

$$S_1 = 4 \times \pi \times r_1^2 \times n_1$$

$$S_2 = 4 \times \pi \times r_2^2 \times n_2$$

$$S_2 = 4 \times \pi \times r_2^2 \times n_1 \times \frac{r_1^2}{r_2^3}$$

$$= 4 \times \pi \times r_1^2 \times n_1 \times \frac{r_1 r_2^2}{r_2^2}$$

$$S_2 = S_1 \times \frac{r_1}{r_2}$$

$$\frac{S_2}{S_1} = \frac{r_1}{r_2} = \frac{c(E_2)}{c(E_1)}$$

From this, it can be estimated that the specific surface (S) and the emulsifier content $c(E)$ correlate inversely with particle radius (r). Based on this model, the following correlations can be drawn:

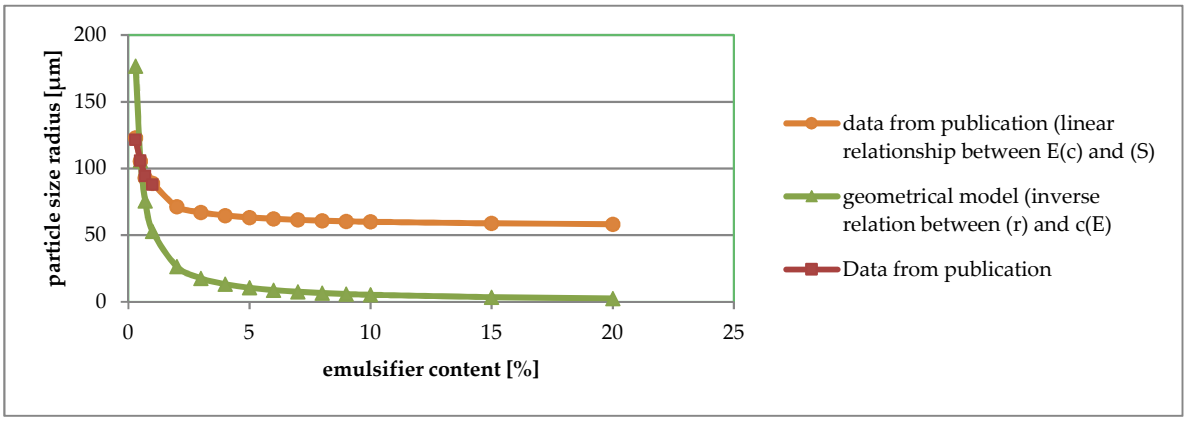

Figure S1. Extrapolation of data points from literature in combination with a purely geometrical model.

From that, it can be estimated that emulsifier percentages >5% would not determine the particle size, due to the non-availability of the emulsifier molecules. This is why we used an emulsifier concentration of 10% in relation to the wax content, to be well above the minimum concentration of 5%.

2. Results Obatined by Turbiscan Lab

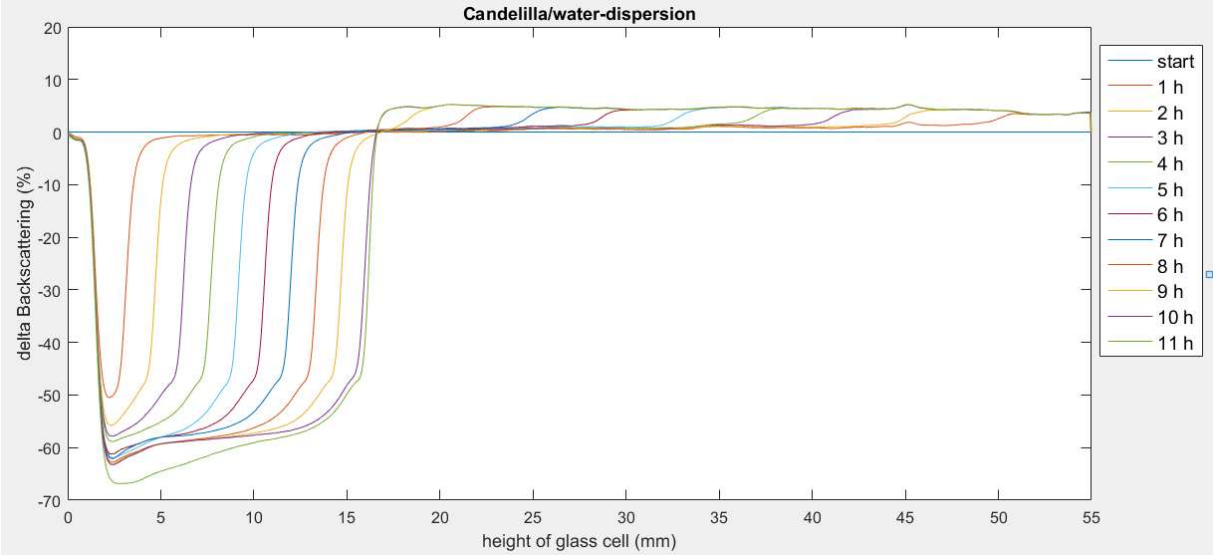

Figure S2. Exemplary measurement result of the phase separation of candelilla wax-in-water suspensions, determined using Turbiscan Lab.

3. Candelilla Wax Composition

Table S1. Fractions of candelilla wax according to various sources.

Fraction	Percentage of the Fraction	Percentage of the Major Chain Length within the Fraction	Major Chain Length	Source
Hydrocarbons	41%	80%	31	[75]
Hydrocarbons	45%–52%	–	–	[76]
n-alkanes	49%–50%	–	29–33	[77]
n-alkanes	–	78.86%	31	[77]
n-alkanes	–	–	31	[78]
n-alkanes (C28–C35)	57.2%	83.9%	31	[79]
n-alkanes (C17–C38)	–	76.9%–80.4%	31	[76]
n-alkanes	~45%	–		[70]
Free acids	8%	48%	30	[75]
Free acids	7%–9%	–		[77]
Fatty acids (C18–C36)	8.3%	38%	30	[79]
Fatty acids (C16–C34)	~30%	–	–	[70]
Alcohol	4%	77%	30	[75]
Alcohol	~25%	–	–	[70]
Alcohol and sterols	12%–14%	–	–	[77]
Monoesters	6%	12%	52	[75]
High-molecular-weight esters	20%–29%	–	–	[77]

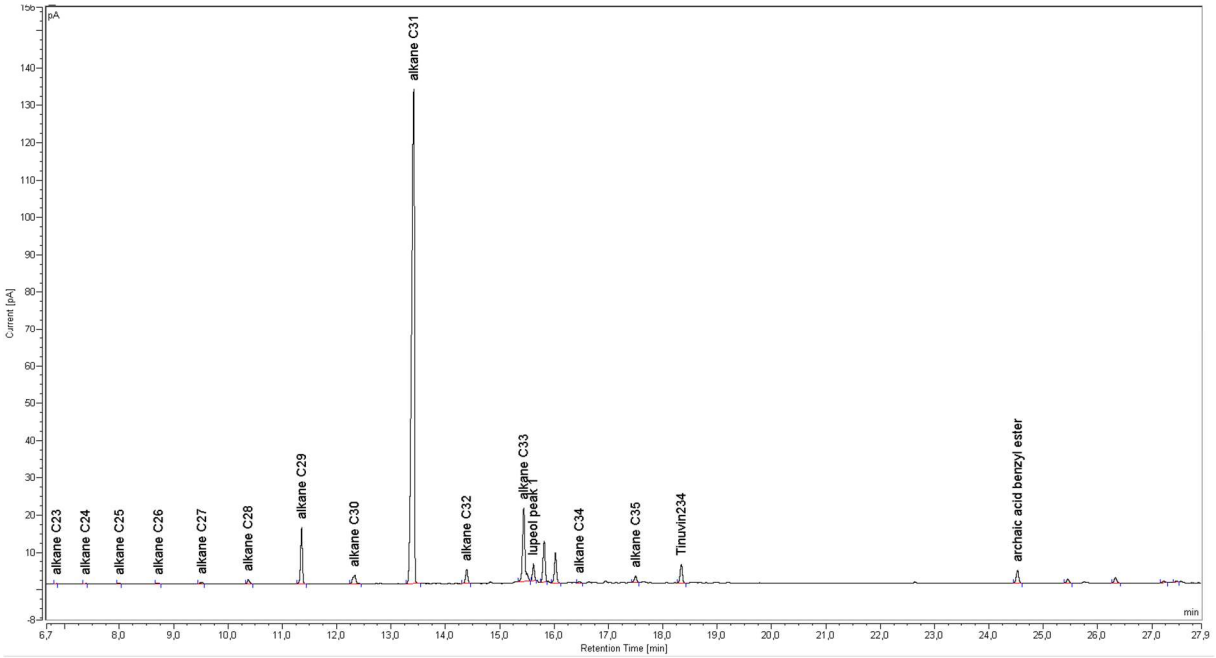

Figure S3. Chromatogram of candelilla wax composition, obtained using gas chromatography.

4. Long-Time Stability of Candelilla Wax-in-Water Suspensions

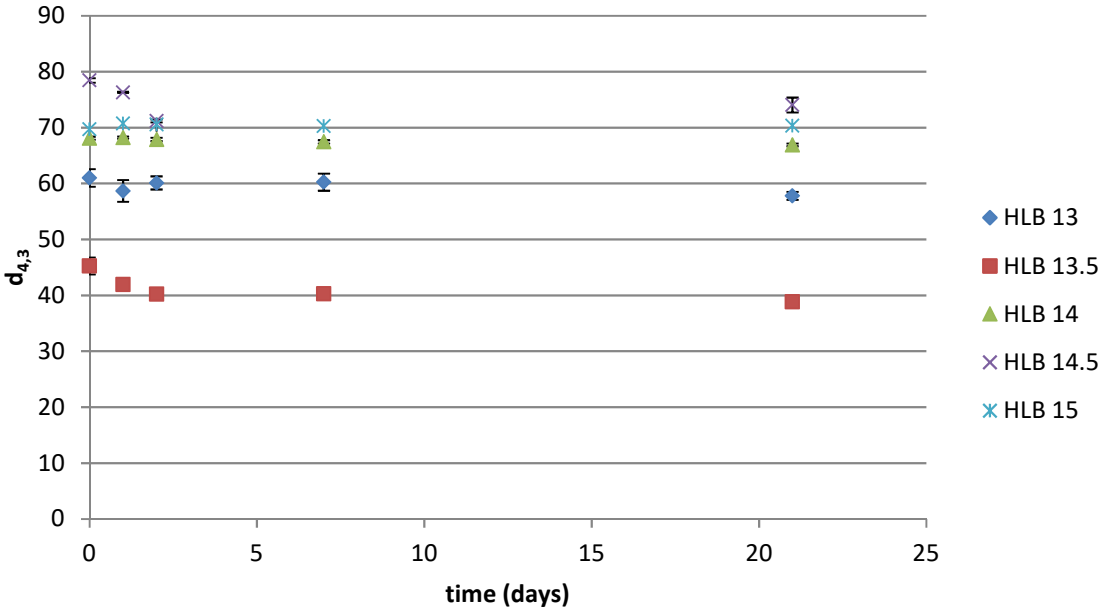

Figure S4. Changes in $d_{4,3}$ over storage time of candelilla wax-in-water suspensions with different HLBs of the emulsifier system.

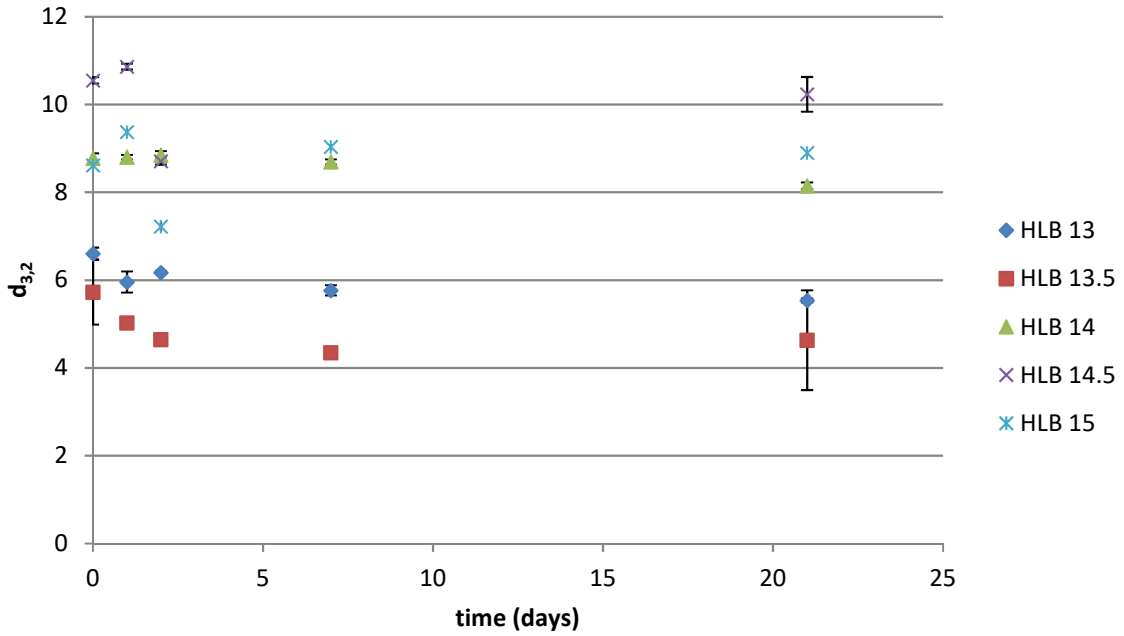

Figure S5. Changes in $d_{3,2}$ over storage time of candelilla wax-in-water suspensions with different HLBs of the emulsifier system.

Table S2. Results of the Spearman's correlation test. The correlation between the HLB value and the change in the particle size ($d_{1,0}$, $d_{3,2}$, $d_{4,3}$) over storage time was examined. Positive correlation ($p < 0.05$, Spearman's rank correlation coefficient > 0) is marked by "+", negative correlation ($p < 0.05$, Spearman's rank correlation coefficient < 0) is marked by "−", no significant correlation is marked by "0" ($p > 0.05$).

HLB-Value	Change of $d_{1,0}$	Change of $d_{3,2}$	Change of $d_{4,3}$
HLB 13	0	−	−
HLB 13.5	−	−	−
HLB 14	0	−	−
HLB 14.5	0	0	0
HLB 15	0	0	0