"PICKERING EMULSIFIERS"

BASED ON SMALL GRANULAR STARCHES

MANUFACTURING AND PHYSICO - CHEMICAL CHARACTERIZATION

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Introduction

Emulsions are mixtures of two immiscible phases where one is dispersed into the other in the form of small droplets. Droplets need to be stabilised at their surface to prevent re-coalescence and thereby a break of the emulsion, see Rayner et al. (1).
Detailed reviews on particle-stabilised emulsions (Pickering emulsions) are given by Binks (2), Aveyard et al. (3), Hunter et al. (4), and, especially for food emulsions, by Dickinson (5,6). Emulsions stabilised by particles are normally more stable against coalescence compared to systems stabilised by surfactants (1,2,3).
The particles – from e.g. hydrophobized small granular quinoa starch – which are bound by Van der Waals forces at the surface of the oil droplets, establish a very stable physical barrier and therefore prevent coalescence of the droplets. The amount of hydrophobized starch, necessary for stabilising an equivalent oil-water interfacial area, is directly proportional to the granule diameter.
Therefore the aim of this study was to prepare hydrophobized **small granular starches** with different degree of substitution (DS) from quinoa, amaranth, and rice by chemical modification with cis/trans 2-Octen-1-ylsuccinic anhydride (OSA) and to determine their physico-chemical properties.

Experimental and results

Preparation of hydrophobized small granular starches

50.0 g of starch was suspended in 200.0 g of distilled water, pH adjusted to 8.2-8.4 and maintained constant during the reaction by addition of 0.1 N NaOH-solution; T = 32.0±0.5 °C. OSA solution in acetone (25.8 g OSA/ 250 ml) was added during 5-40 min and the mixture was stirred for an additional 90 min until the reaction was finished. The amount of OSA in relation to starch dry matter (44.3 g) was exactly 0.6-1.2-1.8-2.4-3.0 % by mass.

Isolation: Repeated centrifugation and washing; two times with water, one time with acetone

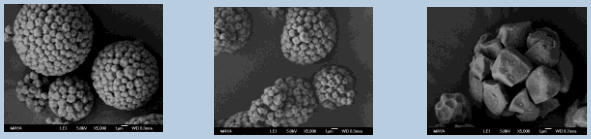
Drying: 48 h at room temperature

DS-determination: 2.000 g of modified starch was suspended in 60 ml of distilled water and the pH was adjusted to 7.0. The OSA groups were hydrolyzed with 20.00 ml of 0.1 N NaOH in a closed Erlenmeyer flask at 35.0±0.5 °C for 24 h. The amount of OSA was determined by titration back to pH 7.0 using 0.1 N H_2SO_4.

Table 1: Degree of Substitution (DS) of OSA-modified small granular starches

Sample	Quinoa starch		Amaranth starch		Rice starch	
	% OSA	DS	% OSA	DS	% OSA	DS
OSA-0.6	0.58	0.0045	0.53	0.0041	0.46	0.0036
OSA-1.2	1.14	0.0089	1.07	0.0083	0.97	0.0076
OSA-1.8	1.67	0.0131	1.50	0.0117	1.40	0.0110
OSA-2.4	2.13	0.0168	2.06	0.0162	1.90	0.0149
OSA-3.0	2.59	0.0205	2.62	0.0208	2.36	0.0186

Physico-chemical properties of the native starches



Quinoa starch — Amaranth starch — Rice starch

Fig. 1: Scanning electron microscopy of native starches

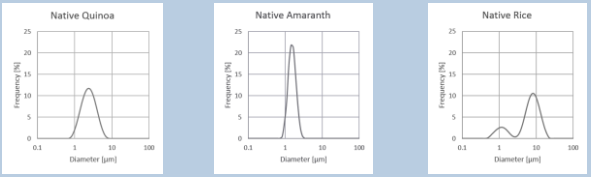


Fig. 2: Particle size distribution of native starches determined by light scattering

Physico-chemical properties of "Pickering emulsions"

Method

- 5 % v/v oil-in-water starch granules stabilized emulsions.
- Miglyol 812 as dispersed phase.
- Phosphate buffer (0.5 mM, pH 7, 0.2 M NaCl) as continuous phase.
- Native starch and different modification levels from 0.6-3.0 % to stabilize the emulsions.
- 7 mL of emulsions were prepared in a glass test tube.
- 50-800 mg of starch/ mL oil was used to stabilize the emulsions.
- Homogenized using a rotor-stator high shear homogenizer (Ystral D-79828, Ballrechten-Dottingen, Germany) with 6 mm dispersing tool, at 22 000 rpm for 30 s.
- Characterizing by using laser light scattering, particle size analyzer (Malvern Inc., UK).

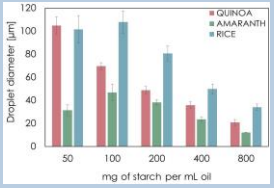


Fig. 3: Volume weighted diameter ($D_{4,3}$) for different types of starches at the same OSA level (3.0 %) as a function of the starch concentration

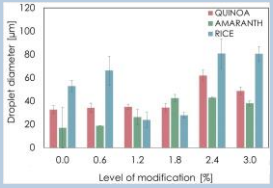


Fig. 4: Volume weighted diameter ($D_{4,3}$) for different types of starches at the same starch concentration (200 mg/ ml oil) as a function of different level of modification

Conclusions

It was feasible to formulate emulsions stabilized by small granular starches. Particularly, surface hydrophobized starches from quinoa and amaranth have a great potential for applications in the food, cosmetic and pharmaceutical industry. Unfortunately these starches are not commercially available.

References

1. M. Rayner, A. Timgren, M. Sjöö and P. Dejmek. J Sci Food Agri 92: 1841-1847 (2011)
2. B.P. Binks. Curr Opin Colloid Interface Sci 7(1-2): 21-41 (2002)
3. R. Aveyard, B.P. Binks and J.H. Clint. Adv Colloid Interface Sci 100-102, 303-546 (2003)
4. T.N. Hunter, R.J. Pugh, G.V. Franks and G.J. Jameson. Adv Colloid Interface Sci 137, 57-81 (2008)
5. E. Dickinson. Curr Opin Colloid Interface Sci 15: 40-49 (2010)
6. E. Dickinson. Interfacial particles in food emulsions and foams, in Colloidal Particles at Liquid Interfaces, ed. by B.P. Binks. Cambridge University Press, Cambridge (2006)

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