Biobased microcapsules improving the converting properties of packaging

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In Szczecin

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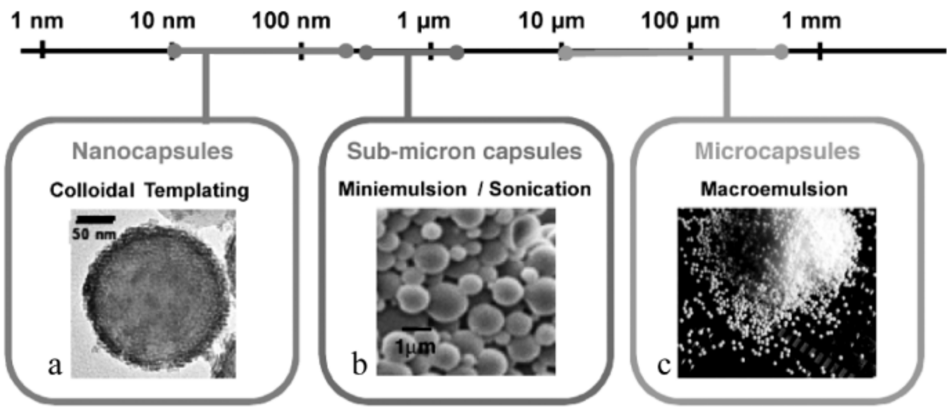
Outlines of presentation

- microencapsulation concept, techniques and applications
- self-healing concept
- microencapsulation systems applied within the project
- properties of microcapsules vs. their „healing capacity"
- conclusions

Microencapsulation is a process by which very tiny droplets or particles of liquid or solid material are surrounded or coated with a continuous film of polymeric material



Nanotechnology roadmap of encapsulation strategies for different length scales
(Wagg D. et al. Adaptive structures: engineering applications. John Wiley & Sons Ltd, 2007, Chichester)

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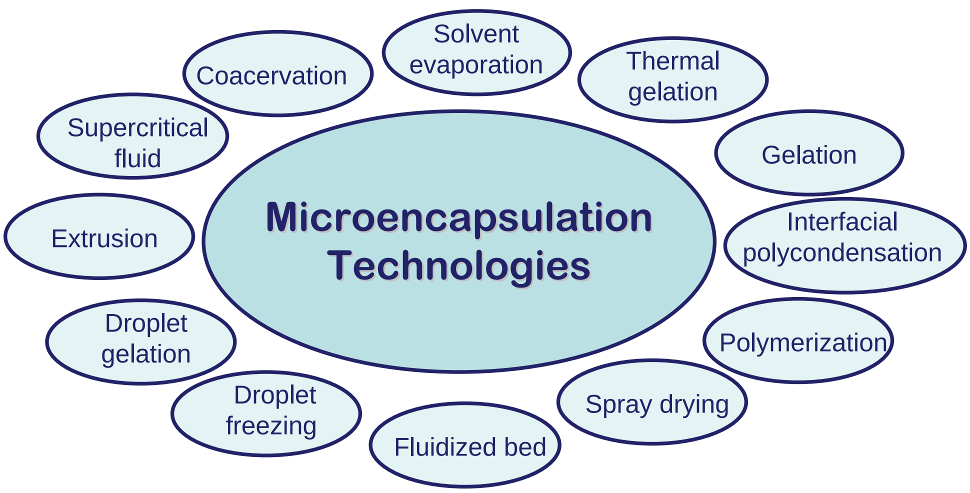
Variety of methods for microencapsulation



Adapted from: www.gate2tech.com

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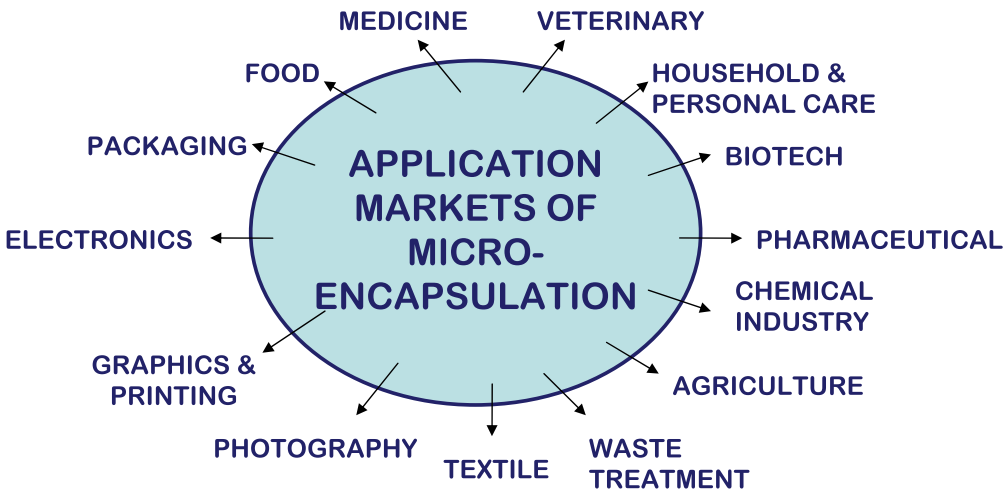
Application of microencapsulation



Scheme with minor modifications taken from: www.gate2tech.com

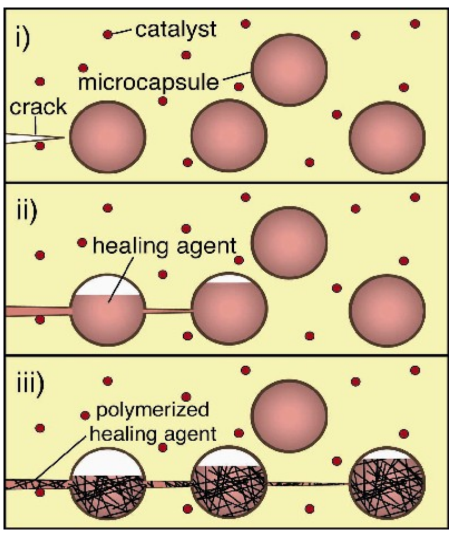
The self-healing concept

A **microencapsulated healing agent** is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent.

(i) Cracks form in the matrix wherever damage occurs.

(ii) The crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action.

(iii) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.



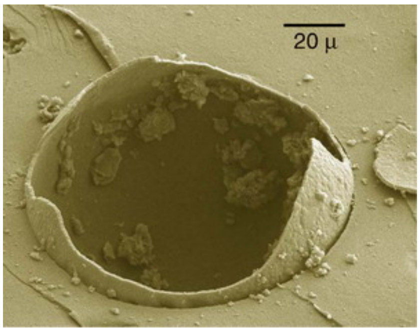
White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, Brown EN, Viswanathan S. Autonomic healing of polymer composites. Nature 2001;409:794–7.

Self-healing polymer composites

There are **three parts of self-healing material** invented at University of Illinois:

Composite material - The bulk of the material is an epoxy polymer composite.

Microencapsulated healing agent - This is the glue that fixes the microcracks formed in the composite material. This healing agent is **dicyclopentadiene** (DCPD).



Scanning electron microscope image of a ruptured microcapsule
Photo: White S. R. et al. Nature 2001; 409:794–7.

Catalyst - In order to polymerize, the healing agent must come into contact with a catalyst. A patented catalyst, called **Grubbs' catalyst**, is used for this self-healing material. It is important that the catalyst and healing agent remain separated until they are needed to seal a crack.

Approximately 20 million tons of composite material is used every year for engineering, defense projects, offshore oil exploration, electronics and biomedicine.

http://science.howstuffworks.com/self-healing-spacecraft1.htm

Self-healing material inspired by nature - rubber tree

The researchers from Fraunhofer Institute in Germany found their inspiration in the **Hevea brasiliensis rubber tree**. Latex from the tree contains **capsules of a special protein** that break open when the bark of the tree is damaged. The protein in the latex then works to seal the wound.

The researchers loaded **microcapsules with a one-component adhesive (polyisobutylene) and put it in elastomers made of synthetic caoutchouc to stimulate a self-healing process in plastics.** If pressure is put on the capsules, they break open and separate this viscous material. Then this mixes with the polymer chains of the elastomers and closes the cracks.

Initial tests on a synthetic rubber by the Fraunhofer research team have indicated that the naturally occurring repair process can indeed be replicated.

http://inhabitat.com/scientists-developing-self-healing-plastics-inspired-by-rubber-tree-plants/

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Preparation and Incorporation of Microcapsules in Functional Coatings for Self-healing of Packaging Board

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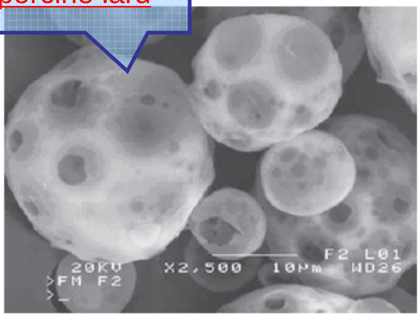
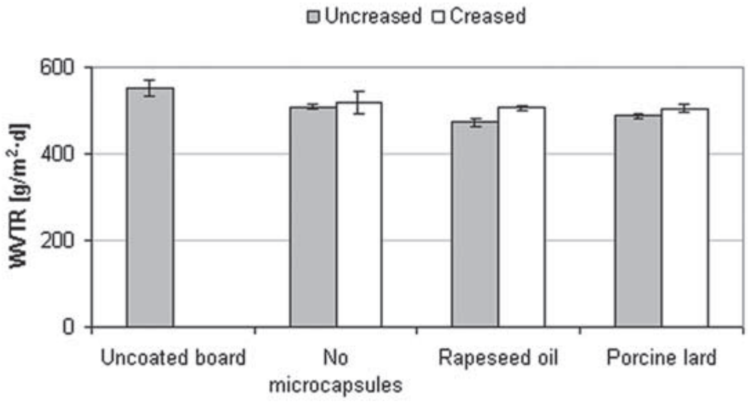
Compounds of microcapsules:

Shell material – ethylcellulose

Core material – rapeseed oil or porcine lard

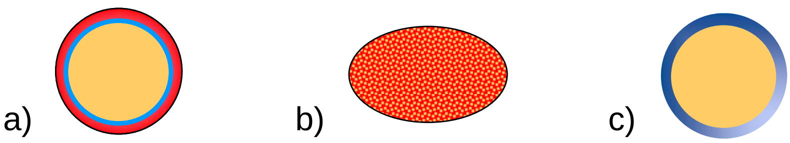


ESEM micrograph showing the porous morphology of microcapsules



Effect of creasing on WVTR for paperboard uniformly coated with and without microcapsules in the pigment coating formulation

Schematic representation of biopolymeric microcapsules investigated in FlexPakRenew project

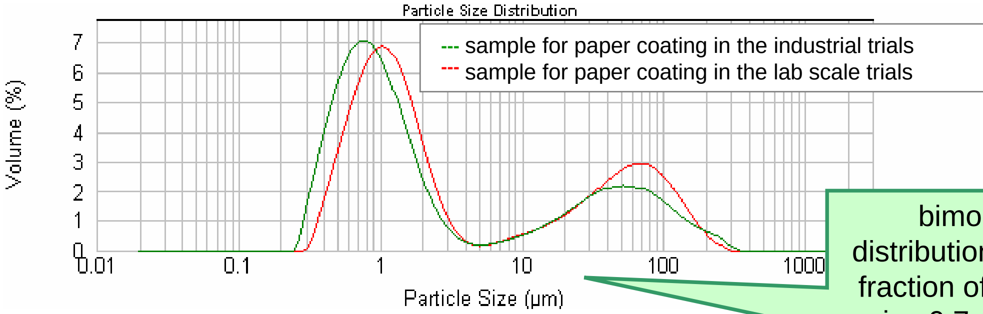


a) Method 1 - polyelectrolyte complex (PEC) microcapsules based on anionic polysaccharides/polymers with multivalent metal cations/cationic surfactants,

b) Method 2 - adsorption/complex formation between starch granules and hydrophobic compounds,

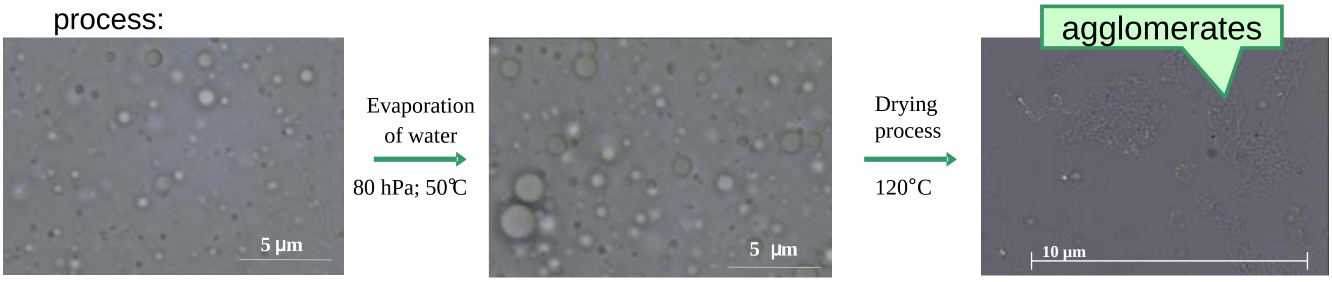
c) Method 3 - coacervation microcapsules based on biopolymers, such as plant proteins and other biopolymers (PLA, EC) using concept of specific interaction on interface by applying high-intensity ultrasound/temperature/non-solvent.

Method 1
Rapeseed oil/alginate PEC microcapsule formation



bimodal particle size distribution with similar volume fraction of capsule of average size 0.7-1 µm and 50-80 µm

The water evaporation under the reduced pressure at 50ºC has allowed to obtain dispersions of solid content 20% with almost the same capsule size distribution before and after the process:



solid content: lower than 5%

solid content: 20%

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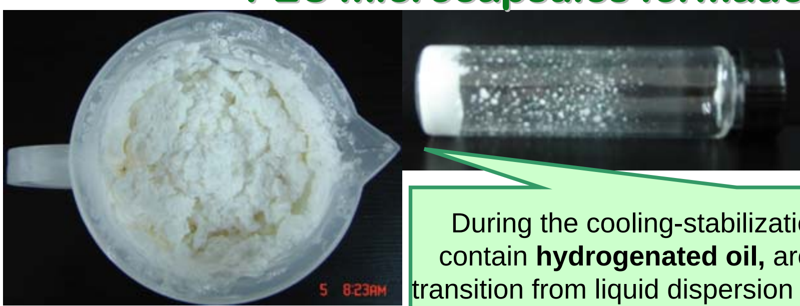
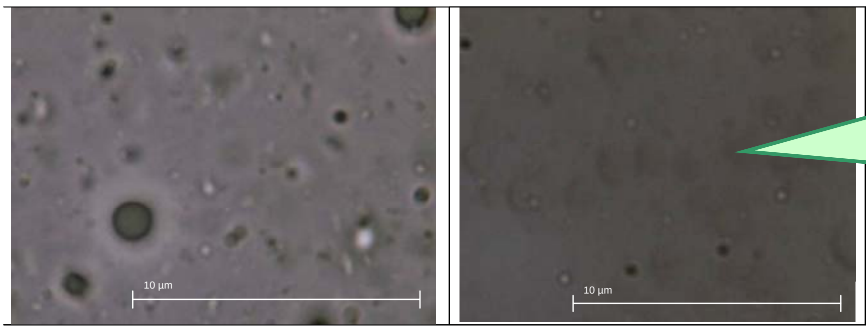
Method 1
hydrogenated oil/alginate PEC microcapsules formation



During the cooling-stabilization process of microcapsules contain **hydrogenated oil,** around 35-40ºC it was observed transition from liquid dispersion towards powder like substance. This process we have called “solid emulsion” formation phenomenon.



aqueous dispersion of microcapsules

microcapsules after drying process at 120ºC

During capsule drying process at high temperature there is a strong tendency to phase separation.

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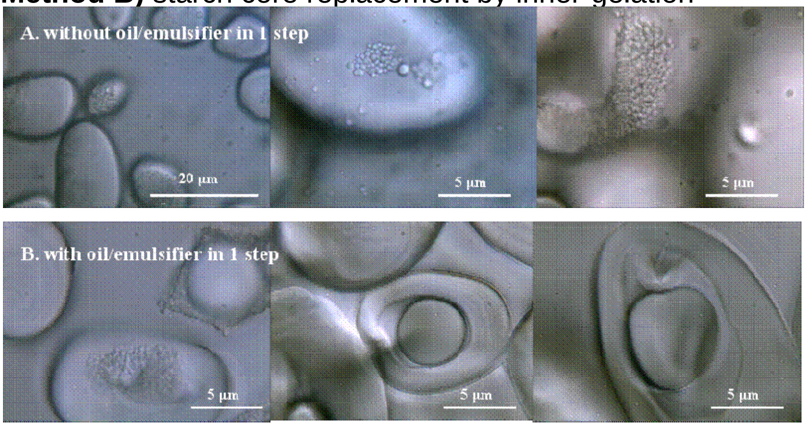
Method 2
Adsorption/complex formation between starch granules and hydrophobic compounds

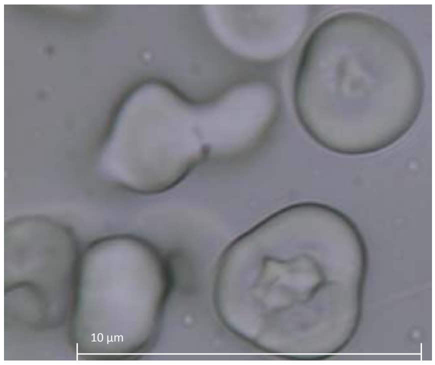
Studies carried out using rapeseed oil as hydrophobic compounds

Two methods of capsule formation based on spray drying technique were applied:
Method A) starch granule surface coacervation
Method B) starch core replacement by inner-gelation



- **Method B** led to higher yield of oil immobilization within the whole helium,
- **Method B** was applied in further experiments carried out using hydrogenated oils as hydrophobic core products

Studies carried out using hydrogenated oils, according to the Method B



- tests with hydrogenated oils have to be applied with temperatures above 60ºC,
- starch gelation process was much faster,
- only some small part of hydrogenated oil can be immobilized within the hilum of starch granules

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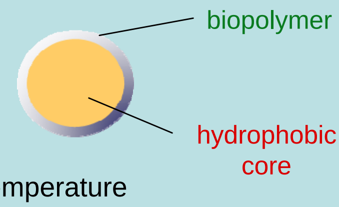
Schematic representation of systems based on Method 3

Method 3

coacervation microcapsules based on biopolymers using concept of specific interaction on interface by applying high-intensity ultrasound + temperature



System 3.1

hydrogenated oils/proteins emulsion

System 3.2

application of blended systems with solvent evaporation technique (PLA + hydrogenated oils/ starch or proteins)

System 3.3

application of hydrophobic phase separation processes - surface coacervation based on ethylcellulose (hydrogenated oils/ ethylcellulose)

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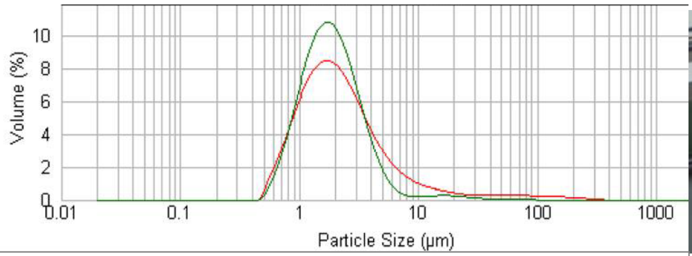
Method 3

System 3.1 - hydrogenated oil/protein emulsions

Particle size distribution

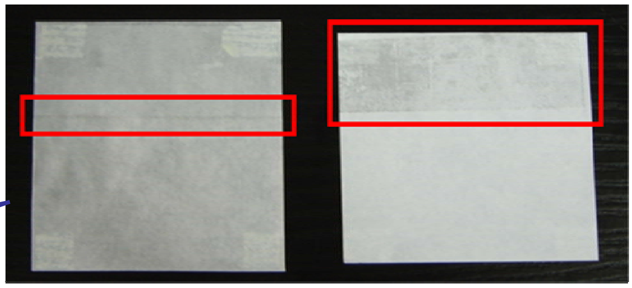


– hydrogenated oil/protein emulsion - sample for industrial trials
– hydrogenated oil/protein emulsion - sample for lab scale trials

Stability of microcapsules

laboratory sealer HSE-3 (RDM, UK)
during compression test

sample after drying process



after drying and compression processes coated papers became transparent as a result of leaking oil

Paper coated with hydrogenated oil/protein emulsion

Uncoated paper ($50\ g/m^2$)

samples after compressing

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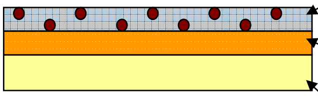
Method 3

System 3.2 – dispersion of the PLA in the biopolymeric systems

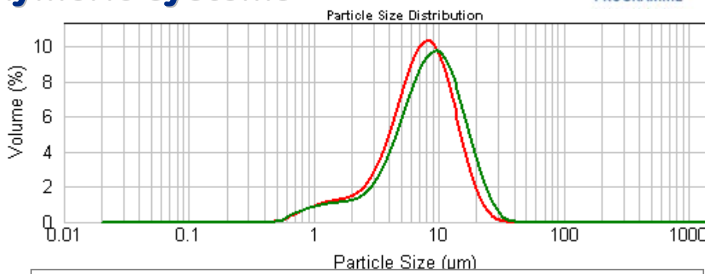
Schematic representation of bilayer films structure:



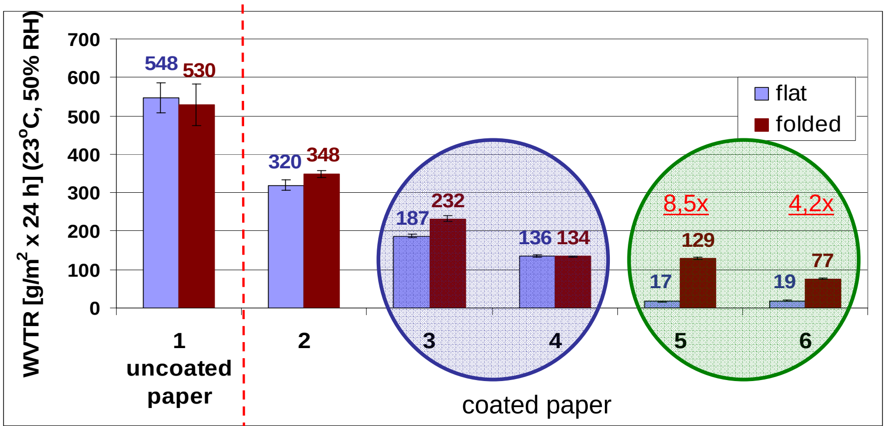
2 nd layer with microcapsules

1 st layer without microcapsules

base paper



---dispersion of PLA+hydrogenated oil/starch microcapsules
---dispersion of PLA/starch microcapsules



1. uncoated paper
2. starch coating
3. dispersion of PLA/starch microcapsules
4. dispersion of PLA+hydrogenated oil/starch microcapsules
5. brittle coating
6. 1 st layer: brittle coating; 2nd layer: dispersion of PLA+hydrogenated oil/starch microcapsules

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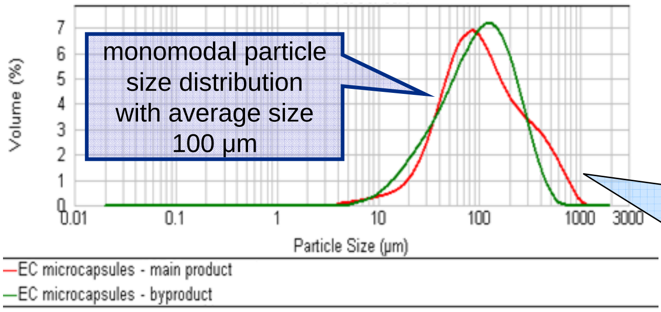
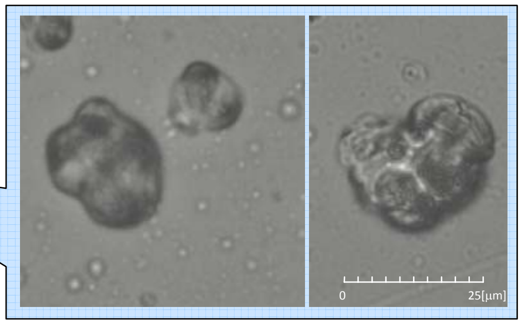
Method 3
System 3.3 - surface coacervation based on hydrogenated oil/ethylcellulose

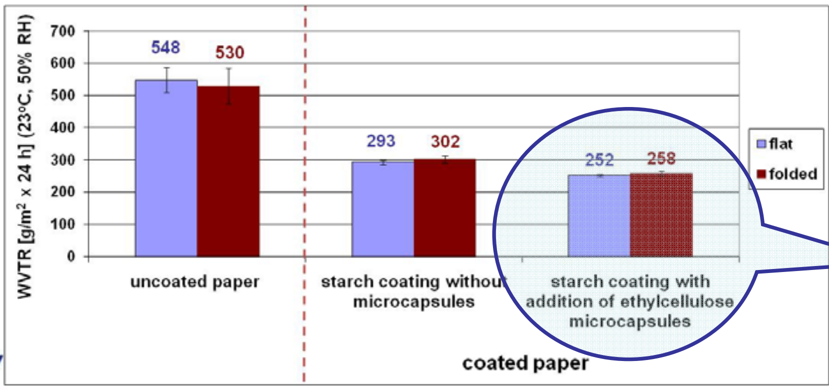
Particle size distribution of microcapsules obtained by spray drying process



Microscopic examination



WVTR examination



Coating without oil signs

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Conclusions

Method No.	Microcapsule system - description, name of components	Advantages	Disadvantages	Final conclusion (+/-)
1.	External gelation using polyelectrolyte complexes (PEC) (alginate)	- all components are on E list (food additives), - new method (PL patent no. 374927 2005), - simple method of formation	- polydisperse in size, - low stability during the drying process, - microcapsules larger than 5 µm	(-) it is impossible to obtain capsules with hydrogenated oils (with melting point above 40°C) smaller than 100 µm capsule with good properties
2.	Adsorption/complex formation between starch granules and hydrophobic compounds (spray-drying)	- application of starch granules as carrier of hydrophobic materials, - easily to scale-up, - product in form of dry powder after spray-drying process.	- microcapsule can change their properties during coating, - low content of encapsulated material in case of surface coated granules and in case of encapsulation of hydrogenated oils with high melting temperatures	(-) it is impossible to obtain capsules with hydrogenated oils (with melting point above 40°C)

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Conclusions

Method No.	Microcapsule system	Advantages	Disadvantages	Final conclusion (+/-)
3.	**Coacervation microcapsules based on biopolymers using concept of specific interaction on interface by applying high-intensity ultrasound + temperature**			
System 3.1.	Hydrogenated oil/protein emulsion	- inexpensive biodegradable material, - similar structure to gelatin based coacervation microencapsulation processes, - possibility of obtaining microcapsules of small size (lower than 10 µm) and narrow particle size distribution	-stability of capsules strongly related to both type of core and wall materials - after drying and compression processes papers coated with hydrogenated oil/protein emulsion became transparent as a result of leaking oil	(-) obtained microcapsules are mechanically unstable
System 3.2.	Dispersion of the PLA in the biopolymeric systems	- system provides self-healing effect of modified paper, - possibility of using asprecoating in metallisation process	- demonstrators possibilities are limited due to the presence of chloroform	(+) it is possible to obtain a stable dispersion of PLA+hydrogenated oil / biopolymer microcapsules
System 3.3.	Surface coacervation based on ethylcellulose	-possibility to obtain a dispersion of microcapsules containing 16% of hydrogenated oil and only 6% of ethylcellulose	- demonstrators possibilities are limited due to system destabilisation after added to aqueous solutions of film-forming polymers - ongoing research related to spray drying are in theprocess	(+) it is possible to obtain a dispersion/powder of hydrogenated oil / ethylcellulose microcapsules

Thank you for your attention!!!

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