Materials for Food Encapsulation - State of the Art Overview

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EPFL - LMRP

COST865 Spring 2008 Meeting
Bioencapsulation Science to Application

Ljubljana, Slovenia
April 25-26, 2008

General requirements

- Certified for food applications: **GRAS** = Generally Recognized As Save
- Able to form a matrix, coating or capsule, to entrap solid, liquid or gas

General functions

- Protection of the core material/active (degradation, reaction)
- Improvement of active handling (conversion of liquid to powders)
- Masking of flavor or odor
- Separation of components (avoid incompatibility)
- Release control (time, location)
- Adjustment of properties (size, color)
- Creation of special effects (visual, by feel, health benefit)

Groups of natural materials for microencapsulation in the food industry

Origin	Carbohydrate	Protein	Lipid
Plant	starch and derivatives cellulose and derivatives gums soluble soybean polysaccharide	gluten (corn) isolates (pea, soy)	fatty acids/alcohols glycerides waxes phospholipids
Marine	gums alginate		
Animal/ Microbial	gums chitosan dextran	caseins whey proteins gelatin	fatty acids/alcohols glycerides waxes phospholipids (shellac)

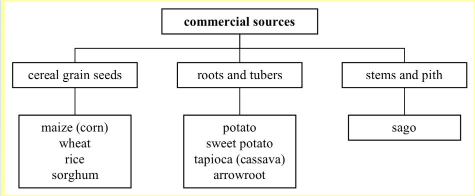
Other suitable materials

- polyvinylpyrrolidone (PVP)
- paraffin
- inorganic materials

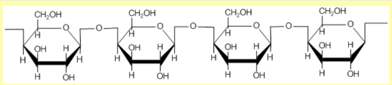
CARBOHYDRATES Saccharides - Polysaccharides

- Homo- and copolymers of sugar residues and/or their derivatives
- Enormous variety occurring in plants, animals, bacteria, fungi, and algae
- Tremendous economical importance
- World consumption exceeds the production of all synthetic polymers.

Starch and starch derivatives - 1

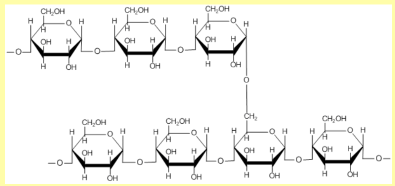


Amylose (20-30%)



- 500 to 6000 units, which form a helix
- Relatively narrow molar mass distribution
- Dssolves in hot water
- Retrogradation and crystallization
- High viscose solutions
- Able to form inclusion complexes

Amylopectin (70-80%)

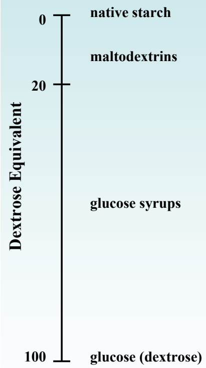


- Up to two million glucose units
- Insoluble in water
- Colloidal suspensions in cold water
- Amorphous powders by drying

CARBOHYDRATES

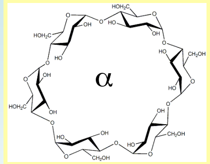
Starch and starch derivatives - 2

Classification of starch hydrolysates based on the DE value

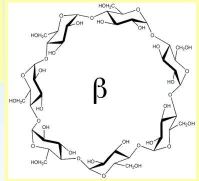


Cyclodextrins

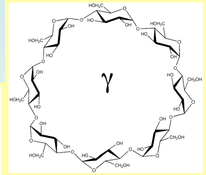
- Cone-shaped rings with a depth of 0.7 nm
- Poor solubility in water
- Form inclusion complexes



- inner Ø 0.5 nm
- outer Ø 1.4 nm



- inner Ø 0.7 nm
- outer Ø 1.5 nm



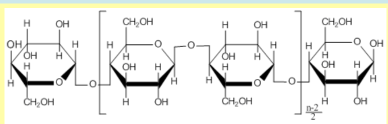
- inner Ø 0.85 nm
- outer Ø 1.7 nm

"Thermoplastic starch" is obtained by destructuring with heat and mechanical forces.

CARBOHYDRATES

Cellulose and cellulose derivatives

Cellulose



- Insoluble in water and other solvents
- Hydroxyl groups are subject of substitution
- Properties of derivatives are:
  - solubility in water
  - thermoreversible gelation
  - film formation ability
  - polyelectrolyte behavior
  - surface activity

Food grade cellulose derivatives

methyl	DS 1.3-2.6
ethyl	DS 2.1-2.6
hydroxypropyl	DR 4
hydroxypropyl methyl	DS(methyl) 0.9-1.8 DR(HP) 0.1-1.0
ethyl methyl	
carboxy methyl (Na)	DS 0.4-1.4
ethyl hydroxyethyl	
crosslinked CMC	

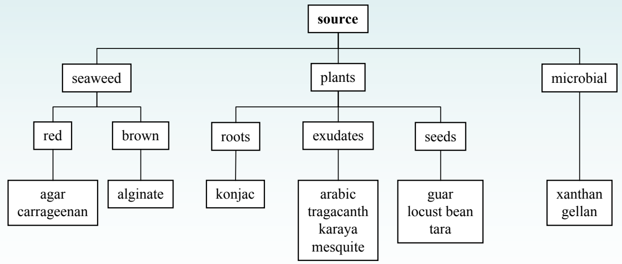
DS: degree of substitution – average number of substituted hydroxy groups per saccharide unit; different information from different sources, widest range taken.
DR: degree of reaction – average number of reagent molecules reacted with one saccharide unit

CARBOHYDRATES

Gums - 1

- Complex macromolecular substances which are either soluble in water or, although insoluble in water, swell while taking up high amounts of water.
- Form viscous solutions or dispersions and are therefore considered as hydrocolloids.
- Some gums are mixtures of oligomers and polymers of different chemical structure and/or chain architecture.

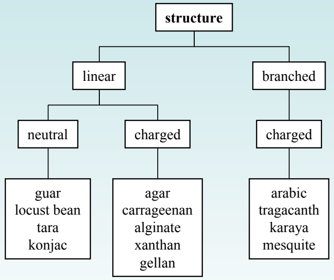
Classification related to the source



CARBOHYDRATES

Gums - 2

Classification related to the structure

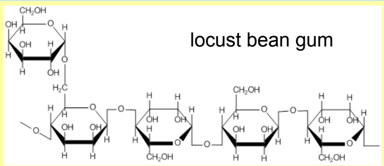


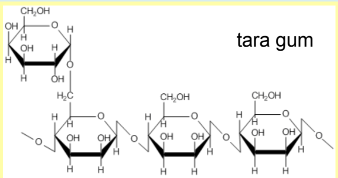
Gums - Plant gums - 1

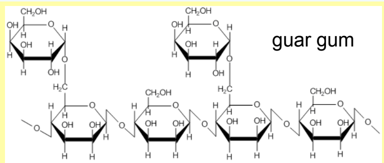
Gummnosis is widespread in the plant kingdom. It results from wounding, heat, drought.
Gums/exudates form a barrier at lesion hindering the invasion of microorganisms.
Only a few plant species are cultivated at present to obtain gums for use in the food industry.
Most often these belong to the Leguminosae family.

gum arabic (GA) (gum acacia)	branched; negatively charged; odorless, tasteless; highly water-soluble with conc. up to 50 wt%; Newtonian solution behavior up to 40 wt%; protective film formation around oil droplets; emulsifier; stabilizer
gum tragacanth	two components: 1) water-swellable component – **bassorin** 2) water-soluble component – **tragacanthin** branched; negatively charged; one of the most acid-resistant gums; bi-functional emulsifier; viscous solutions even at low conc. pseudoplastic; protective film formation around oil droplets
gum karaya	branched; negatively charged; one of the least soluble of the exudates gums (10 % in cold water, 30% in hot water)
mesquite gum	branched; negatively charged; solubility comparable to GA, but steeper increase of the viscosity; good film formation
galactomannans - LBG, tara, guar	linear; neutral; different solubility: guar gum > tara gum > locust bean gum (LBG); pseudoplastic solution behavior
pectin	soluble in water; low viscosity compared to other gums; at low conc. Newtonian at higher conc. pseudoplastic solution behavior; non-permanently charged; complicated gelation behavior

Gums - Plant gums - 2





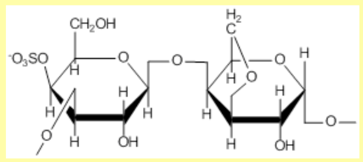


Gums - Marine gums - 1

Selected properties of **carrageenans**

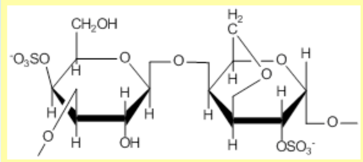
property	carrageenan type		
	kappa	**iota**	**lambda**
solubility in hot water	T > 70°C		soluble
solubility in cold water	Na-salt soluble; from limited to high swelling of K-, Ca-, and ammonium salts	Na-salts soluble, Ca-salts give thixotropic dispersions	all salts soluble; viscous pseudoplastic solutions
gel formation	thermo-reversible gels on cooling in the presence of appropriate counterions		non-gelling
gelation	strongest with K	strongest with Ca	
gel type	brittle with syneresis; poor freeze-thaw stability	elastic, no syneresis; good freeze-thaw stability	
pH stability	stable at neutral alkaline pH; pH=3.5: hydrolysis of solutions but gels are stable		hydrolysis below pH 4.3
salt tolerance	poor	good	good

Gums - Marine gums - 2

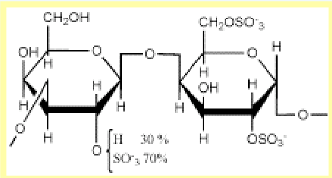


kappa - carrageenan

iota - carrageenan



lambda - carrageenan

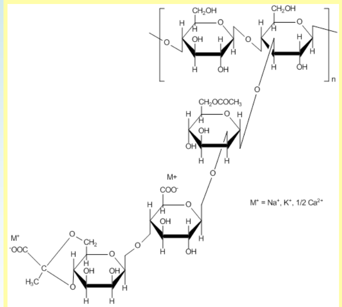


CARBOHYDRATES

Gums - Animal/Microbial gums

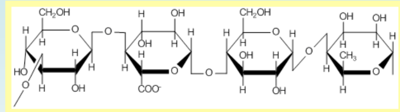
Polysaccharides biotechnologically produced by bacteria are biopolymers with novel and and partially unique functional properties.

Principal chemical structure of xanthan gum



- High molar mass anionic PEL soluble in cold water
- Solution viscosity stable over wide range of pH and T
- Unusual: addition of salt increases solution viscosity
- Cryogelation

Principal chemical structure of gellan gum



- High molar mass anionic PEL
- Different degree of esterification possible
- Stable until 120°C
- Viscosity increases with the degree of acetylation
- Thermo-reversible gelation
- Gel texture depends on the degree of acetylation

CARBOHYDRATES

Soluble soybean polysaccharide (SSPS)

Chemistry

- Chains composed of a number of different sugar units of different quantity.
- Negatively charged units are located in the polymer backbone, anionic PEL.
- Short side chains contain neutral sugar units.

Origin

- Extracted from okara, the residue after oil and soy protein extraction from soybean.

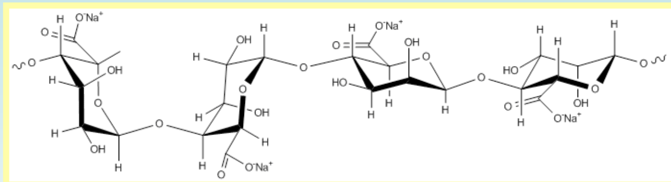
Properties

- Soluble in cold and hot water yielding solutions of relatively low viscosity.
- SSPS solution do not gel.
- Excellent adhesion and film forming properties.
- Films are colorless, transparent, water-soluble.
- Prevent oxidation of oils.
- Can be used as emulsifier and stabilizer for emulsions.

CARBOHYDRATES

Alginate

Principal chemical structure of alginate



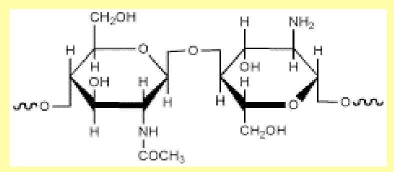
G M

- Linear anionic polyelectrolyte.
- Solubility in water depends on the type of the counterion.
- Viscous solutions showing Newtonian and pseudoplastic behavior dependent on concentration and shear rate.
- Hydrogel formation with multivalent counterions and positively charged PEL.
- Alginate powder and solutions are subject to chain degradation if not appropriately stored.

CARBOHYDRATES

Chitosan

Principal chemical structure of chitosan



- Non-permanently charged cationic polyelectrolyte, pK_a about 6.5.
- Soluble in acidic to neutral medium influenced by the degree of acetylation.
- Forms hydrogels with alginate and tripolyphosphate.
- Very good film forming ability.

PROTEINS

Natural macromolecules composed of linear chains of amino acids.

Gluten

- Complex mixture of
  - **gliadins** (monomeric gluten proteins) and **glutenins** (polymeric gluten proteins)
- **Gliadins:** soluble in distilled water but aggregate in salt solution.
- **Glutenins:** very low solubility in water.
- Gliadins have higher ability than glutenins to reduce the surface tension.
- Elastic film formation

Milk proteins - 1

Casein fractions and some characteristics typical for bovine milk

parameter	caseins			
	α_{s1} - casein	α_{s2} - casein	β - casein	κ - casein
conc. %	0.9 – 1.5	0.3 – 0.4	0.9 – 1.1	0.3 – 0.4
isoionic pH	4.94	5.45 – 5.23	5.14	5.61
molar mass $\times 10^{-4}$ g/mol	2.36	2.52-2.54	2.4	1.9

Whey protein fractions and some characteristics typical for bovine milk

parameter	whey proteins			
	α - lactalbumin	β - lactoglobulin	immunoglobulins	serum albumin
conc. %	0.07 – 0.15	0.2 – 0.4	0.06 – 0.1	0.01 – 0.04
isoionic point	4.2-4.5	5.2		5.3
molar mass $\times 10^{-4}$ g/mol	1.4	1.8	15-90	6.6

Ennis et al. in: Handbook of hydrocolloids, 2000, pp. 189-217

Milk proteins - 2

Caseins

- Extremely heat stable proteins, do not coagulate by heat.
- Insoluble at their isoelectric point, at about pH 4.6.
- Solubility varies with the pH.
- Good surface active properties.
- Good fat emulsifiers
- Water vapor permeability of films depends on the protein type.

Whey proteins

- Globular proteins
- Soluble in the ionic environment of milk
- Become insoluble at their isoelectric point ot about pH 5 at very low ionic strength.
- Denature at temperatures above 70°C.
- Form thermally irreversible gels of different quality.
- Good surface active properties.
- Films formed by thermally induced disulphide cross-linking are excellent gas barriers.
- Cold gelation occurs by adding calcium to a preheated mixture.
- Continuous and homogeneous membranes by self-aggregation around oil droplets.

Gelatin

- Heterogeneous mixture of single or multi-stranded polypeptides.

- Pure form: translucent brittle solid substances, colorless or slightly yellow, almost tasteless and odorless.
- Melt when heated and solidify when cooled again.
- Dissolves on hot water and gels on cooling below 35-40°C, thermo-reversible gels.
- Also soluble in most polar solvents.
- Gelatins are amphiphilic,

- The quality and properties depend on the process of manufacturing:

- type A gelatin is obtained by acidic treatment of collagen - isoelectric point pH 7 to 9.4
- type B gelatin is obtained by alkaline treatment - isoelectric point pH 4.8 to 5.5

- Good emulsifying properties.
- Can form hydrogels by PEL complex formation with both anionic and cationic PEL.

- Gelling properties of warm-blood animal are superior to fish skin gelatin.

LIPIDS

- Characteristic for lipids is their general insolubility in water; they are hydrophobic.
- Lipids involve molecules and substances of large diversity and structural variety.
- Examples are: oils, fats, waxes, phospholipids.

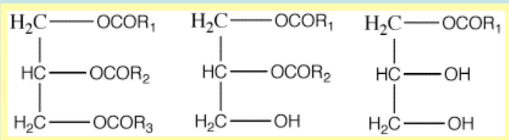
Fatty acids and fatty alcohols

- Two subgroups of fatty acids:
  - saturated acids, monocarboxylic acids of the overall formula $CH_3(CH_2)_nCOOH$
  - unsaturated acids, having one or more double bonds in the chain.

- Fatty alcohols: a hydroxyl group has replaced the carboxylic group.

- Solubility and melting point of fatty acids vary with chain length.
- Fatty alcohols behave as nonionic surfactants and have emulsifying properties.

Glycerides



tri   di   mono

- Di - and monoglycerides have emulsifying properties.
- The melting points strongly depend on the chemical nature and the symmetry.

Waxes

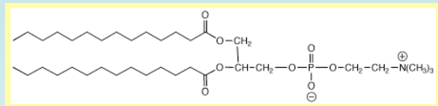
- Waxes are esters of fatty acids. In contrast to fats and oils, the fatty acids are not esters of glycerol but of higher primary monovalent alcohols.

  Beeswax: melts in the range 62 to 64 °C
  Carnauba wax: one of the hardest natural waxes; melts in the range 78 to 85°C.
  Candelilla wax: not as hard as carnauba wax; melts in the range 67 to 79°C.

- The waxes are compatible with each other and most oils, fatty acids, glycerides, hydrocarbons.

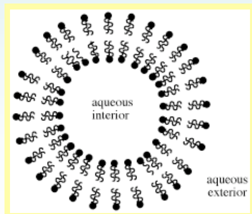
Phospholipids - Liposomes

Phospholipids



- Ionic amphiphiles - betains
- Emulsifiers and dispersing agents
- Lecithin (phosphatidylcholin) is the most abundant, where the base is cholin.

Liposome



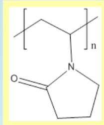
- In water: phospholipids aggregate or self-assembly into well organized and defined structures - bilayers, which can be forced to form liposomes.
- Liposomes are kinetically stable but not thermodynamically.

- Important parameter:
  - ***gel to liquid crystalline transition temperature***

Others

Polyvinylpyrrolidone (PVP)

- Synthetic neutral polymer
- Soluble in water and organic solvents
- Aqueous solutions exhibit Newtonian behavior.
- Good film formation ability
- Good temperature stability of coatings



Paraffin

- Family of linear hydrocarbons with the general formula C_nH_{2n+2}
- Paraffin wax, the solid form, has n > 20. It is white, odorless, tasteless.
- Edible but not digestible.
- Melting point range from 48 to 95°C, dependent on n.

Shellac

- Secreted by the lac insect *Laccifer lacca (Kerria lacca)*.
- Exact chemical composition is unknown (probably a network of various acid esters).
- Coatings obtained from alcoholic solutions are of superior durability and hardness.
- Edible.

Inorganic materials

- Tripolyphosphate
- Silicon oxides
- Aluminum oxides
- Calcium carbonate

Materials Properties

Primary characteristics - molecule properties

- Chemical composition
- Molecular architecture
- Molar mass, molar mass distribution
- Homogeneity, heterogeneity

Secondary characteristics - substance properties

- Solubility
- Rheology of solutions and melts
- Film formation ability, film quality
- Surface activity
- Stability, durability, degradability
- Melting point, boiling point, glass transition temperature

Knowledge of the relationships between primary and secondary characteristics supports the goal-directed design, development and optimization of encapsulates.

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Applications - 1

Material	Application	Technology
maltodextrin, gum arabic, modified starch	instant beverages, confectionary, instant desserts	spray drying, fluidized spray drying
	tea, chocolate fillings, pretzels	compacting
	instant beverages	agglomeration
	chocolate, instant soups and sauces, instant beverages, tea	continuous fluidized bed granulation, rotor granulation
maltodextrin, modified starch	chocolate, instant soups and sauces, instant beverages, tea	extrusion
hydrogenated oil, fractionated vegetable oil	any moist food with heat treatment	spray chilling
cyclodextrrin	top note protection	molecular inclusion
gum arabic, gelatin	chewing gum, instant soups and sauces, baked goods	coacervation
alginate	chewing gum, confectionary	free nozzle
gelatin	chewing gum, confectionary, instant soups and sauces, instant beverages	submerged nozzle

adopted from J. Uhlemann et al. symrise, 2008

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Applications - 2

Active	Material for encapsulation	Reference
vitamin C, acerola, synthetic ascorbic acid	a) maltodextrin of DE20 mixture DE20/gum arabic (GA); b) maltodextrin DE25, GA, or mix of both	a) Righetto, 2006 b) Righetto, 2005
vitamin C	tripolyphosphate/chitosan	Desai, 2005, 2006
vitamin E	starch	Chen, 2004
vitamin A acetate dissolved in coconut oil	Hi-CAO 100 (starch octenylsuccinate, OSA-starch)	Xie, 2007
conjugated linoleic acid (CLA)	whey protein concentrate (WPC), gum arabic (GA), blend WPC/maltodextrin 10DE (1:1, w/w)	Jimenez, 2006
linoleic acid	gum arabic	Fang, 2005
European pear aroma	α-cyclodextrin (CD), GA, soybean soluble polysaccharide (SSPS), highly branched cyclic dextrin (HBCD)	Tobitsuka, 2006
	cyclodextrins	Tobitsuka, 2005
oregano, citronella, and marjoram flavors	milk-protein based matrices: WPC, skimmed milk powder (SMP)	Baranauskiene, 2006
Bifidobacterium lactis	hydrated gellan, xanthan gums	McMaster, 2005
Bifidobacterium PL1	starch	O'Riordan, 2001
probiotic bacteria *L. acidophilus* *B. lactis*	alginate/Hi-Maize™ starch	Kailasapathy, 2006
probiotics, *L. acidophilus 547* *B. bifidum ATCC 1994, L. casei 01*	alginate/$CaCl_2$/chitosan	Krasaekoopt , 2006

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Applications - 3

Active	Material for encapsulation	Reference
B. breve R070, B. longum R023	milk fat, denaturated whey proteins	Picot, 2004
lactobacillus sp.	gum arabic (GA), gellan gum (GG), mesquite gum (MG), and binary mixtures thereof	Yáñez-Fernánandez, 2007
lipids	various polysaccharides	Kikuchi, 2006
lipids: oleic acid, linoleic acid, stearic acid	potato starch, waxy maize starch, tapioca starch	Kapusniak, 2006
vegetable oil	maltodextrin/GA, 3/2, w/w	Fuchs, 2006
fish oil	a) modified cellulose, skim milk powder, mixture of fish gelatin/corn starch b) methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), maltodextrin	a) Kolanowski, 2007 b) Kolanowski, 2004
	modified starch	Tan, 2005
tuna o/w emulsion	lecitin-chitosan, corn syrup	Klinkesorn, 2006
ferrous sulfate + ascorbic acid	liposomes	Kosaraju, 2006
iron (ferric pyrophosphate), iodine (potassium iodate), vitamin A	hydrogenated palm fat	Wegmüller, 2006
chitooligo-saccharide	polyglycerol monostearate (PGMS)	Choi, 2006
anthocyanin pigments of black carrot	maltodextrins: DE 10, DE 20-23, DE 28-31	Ersus, 2007
isoflavone, β-galactosidase	medium-chain triacylglycerol (MCT), polyglycerol monostearat (PGMS)	Kim, 2006
allyl isothiocyanate –AIT (pathogeness inhibitor)	gum arabic	Chacon, 2006

Acknowledgements

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Redouan Mahou
Ingrid Margot