Use of Nanomaterials to Improve Food Quality and Food Safety: Nutrient Encapsulation and Food Packaging

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Nanotechnology in Food Products:
Impact on Food Science, Nutrition and the Consumer
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Applications of Nanotechnology in Food Science and Technology

- Food Science & Technology
  - Processing
  - Structures
  - Materials
  - Food Science & Technology
  - Food Safety & Biosecurity

- Nano-particles
- Nano-emulsions
- Nano-composites
- Nano-structured materials
- Nano-sensors
- Nano-tracers

- Ingredient/Packaging
  - Delivery
  - Formulation
  - Packaging

- Laboratories
  - Heat/Mass transfer
  - Nano-scale reaction eng.
  - Nano-Biotechnology
  - Molecular synthesis
Functional Nanostructures

- Microemulsions
- Liposomes
- Nanoemulsions
- Particles
- Fibers
- Monolayers
A. Monolayers & Nanoclay Composites

- Inert Monolayers
- Protein
- Carbohydrates
- Clay
- or synthetic polymers
- Microphase separated
- Intercalated
- Exfoliated
- Torturous
- Path
- Reduced O₂ and H₂O transmission
- Microwavable
- Increased mechanical strength

Other (migrating/nonmigrating) structures are now included
Next Steps: Nanometer Thick Monolayers as Protective Coatings

Droplets
Particulates
Biopolymers
Association Colloids
Polar Lipids
Lipid Bilayers

McClements, 2008

Single or multiple monolayers can be build up by sequential addition of adsorbing materials. Layers can consist of droplets (e.g. nanoemulsions), particulates (nanoparticles), polymers, association colloids, polar lipids or bilayers.
B. Microemulsions

- Microemulsions are ‘thermodynamically stable’. In contrast to emulsions.
- They are isotropic solutions that are typically transparent.
- Like emulsions, their stability can be influenced by addition of salt, other additives, temperature or pressure.
- Microemulsions can be prepared from milky emulsions by addition of short chain alkanols or by addition of oil to a mixed surfactant system.
- As such they are three or four component systems:
  - Water/amphiphile/oil
  - Water/surfactant/co-surfactant/oil

Example of a ternary phase diagram of water-oil-surfactant mixtures

Current Science, 2001, Vol. 80, pp.990-1002
General Applications of Microemulsions

• Non-Food Applications:
  – Enhanced Oil recovery
  – Fuels
  – Lubricants & Corrosion Inhibitors
  – Coatings & Textile Finishes
  – Cosmetics
  – Agrochemicals

• Food Applications:
  – Solubilization of Food Ingredients
  – Improved reaction efficiencies e.g. interesterification, hydrogenation
  – Extraction technologies
  – Protective wax coatings
  – Food gels

Key issue: TAG solubilization → TAG itself is slightly surface active, and thus not capable of forming separate oil domains in the way mineral oils do. Thus very limited choice of components to form TAG microemulsion
Antimicrobial Efficacy of Simple Microemulsion (Eugenol – Surfynol) Against *E. coli*

Growth of (a) *Escherichia coli* O157:H7 H1730 in the presence of Surfynol® 465 with eugenol (b) *Escherichia coli* O157:H7 932 in the presence of Surfynol® 485W with eugenol.

Some Surfactant Specificity in Terms of Activity
High Activity Against Biofilms

Cell numbers (log CFU/cm²)

Time (min)

Control

Loaded Micelles

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Progress Timeline in the Design of “Antimicrobial” Microemulsions

1999-2003
- Nonionic Surfactant

2003-2006
- Anionic Surfactant
- Cationic Surfactant

Simple Micelle

Lipid Antimicrobial

Simple Antimicrobial Microemulsion

Binary Micelle (may already be antimicrobial)

2006-now
- Binary Microemulsions

May be DOUBLE !!!

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Superior Performance of Mixed Microemulsions

Cationic Micelles

Cationic – Nonionic Micelle

4°C/12 h

Room temperature

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Next Steps - Composite Systems: Microemulsion & Polymer Clusters

Charged Binary Microemulsion

Mixing at appropriate conditions and concentrations

Charged Food Polymer (e.g. Pectin)

Stable Cluster with Potentially Improved Functionalities (Antimicrobial, Sensory)

Inappropriate conditions

Aggregation & Precipitation
B. Liposomes: Using Polar Lipids as Building Blocks

- Spherical membrane structure (bilayer)
- Base materials (phospholipids) widely available in nature
- Materials digestible
- Good interactions with cell membranes
- Internal pH and electrolyte concentrations adjustable
- Suitable for both lipophilic and hydrophilic compounds
Structures and Composition of Liposomes

- Spherical lamellar bilayers composed of lipid molecules
  - Hydrophilic Headgroups: Charged or Neutral
    - Phosphatidyl choline, -glycerol, -ethanolamine
  - Hydrophobic Fatty Acids Can Vary According to:
    - Chain length (14, 16, 18 C)
    - Saturated/Unsaturated (18:0, 18:1, 18:2)
- Structures
  - Small/Large Unilamellar Vesicle (SUV/LUV)
  - Multiple Layer Vesicles (MLV)
  - Multiple Vesicular Vesicles
Encapsulation of Food Antimicrobials – Activity in Milk -

- Higher activity of encapsulated nisin in disk diffusion assays
- Functionality influenced by choice of phospholipids
- Bacteriostatic activity in milk
- Unencapsulated nisin initially bacteriocidal but rapidly loses efficacy

Under investigation:
- Delivery of w-3 fatty acids, color and water-soluble vitamins
- As fat replacers
Next Steps: Nanoscalar Engineering: Double-Layered Liposomes

Nisin, Lysozyme

Phospholipid & Buffer

Isotropic Solution

Microfluidize

Primary Liposomes

Ultrafiltration

Add Protein or Carbohydrate

Secondary Liposomes

Unilamellar Liposomes

Nisin or Lysozyme

Two Layers

Decreased Leakage

Improved salt stability

Controlled Release

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1. Stable secondary liposomes are formed within a narrow window of chitosan to liposomes concentration ratios. Below and above the critical ratio, bridging flocculation and depletion flocculation may occur.

2. Secondary liposomes are significantly more stable to long-term storage and may repel positive metal catalysts causing oxidative damage.

**Addition of adsorbed layer changes surface properties and size \(\rightarrow\) altered functionality**
C. Biopolymeric Nanoparticles

- Biopolymer Nanoparticles
  - Solid Particles with diameters < 100 nm
  - Basis of modern anti-cancer drug delivery systems
  - Extremely high bioactivity
  - Als carrier of antimicrobial components:
    - As part of the particle matrix structure
    - Adsorbed at the surface (direct oder via linker molecule)

**Activity against E. coli O157:H7 without nisin**

**Activity against E. coli O157:H7 with nisin**

ORGANIC SOLVENTS! Deadend…
D. “Solid Lipid Nanoparticles” (SLN)

- Liquid lipid in emulsion is replaced by high melting point lipid
- Glycerides or waxes suitable
- Typical medium size ranges from 50 - 500 nm
- At small sizes, crystal structures become dependent on surfactant and size
- Highly effective carrier systems for susceptible bioactive ingredients

![TEM of SLN Preparation after 1 year storage](image)


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Stability of β-Carotene in SLN

- Example of a susceptible lipophilic bioactive encapsulated in SLN
- Interfacial engineering key to success
- Surface initiated crystallization via saturated (hydrogenated) lecithin used at the interface
- Generated crystal structure initiated from surface better at incorporating carotene
- Much improved chemical stability

Helgason, Kristbergsson, Decker, McClements & Weiss 2008, JAFC, Submitted
Next Steps? Colloidsomes with SLN

- Solid particles can be used as the basis for the formation of shells around emulsion droplets
- Emulsion may be loaded with bioactive
- Application of heat may lead to a fusion of nanoparticles
- Porosity of shell could be adjusted by varying particle size
- Release upon application of mechanical/thermal stress

D.A. Weitz Laboratory, Harvard,
E. (Biopolymer) Nanofibers

$V_{\text{max}} \sim 10 \text{ m/s, } a \sim 400 \text{ g}$

- The polymer solution is being pumped to the capillary $\rightarrow$ positively charged polymer solution with high charge densities.
- At high applied voltages, the electrostatic repulsions is able to overcome the surface tension, resulting in expulsion of a jet (>10kV).
Electrohydrodynamically Sprayed Nanoparticles

- Uniform particles produced under various conditions
- A & B: Uniform particles ~2.5 um by spraying 5 wt% PLG in acetone (8 kV)
- C & D, PLG in methylene chloride, 15kV
- E & F, PLG in acetonitrile, 10 kV,
- C,D,E,G approx. 80 – 200 nm in size

Berkland et al, 2004
Antimicrobially Active Chitosan – PVA Filters

- SEM images of Chitosan – PVA structures after electrospinning (5 wt%)
- Variable Chitosan – PVA ratio
- Process conditions: 22 kV (17 μA) with source-target distance of 15 cm
- No fibers with pure chitosan
- Fibers with increasing fiber diameter with increasing concentration of PVO

Wongsasulak, McClements and Weiss, Polymer, 2007
Porous Nanofibers

- Example: Polystyrene (collaboration with University of Tennessee)
- Under appropriate processing conditions, production of porous fibers possible
- Ideal materials for catalysis due to extremely high surface-volume ratio and good mass transport
- Enzyme Immobilization
Microemulsions were incorporated in solutions to produce spun fibers. Fibers were thus rendered antimicrobially active → Packaging or ingredient system.
The Future of the Science: Playing Lego with Molecules
- Composite Nanostructures – The Sky is the Limit -

Liposomes  
Solid Lipid Nanoparticles  
Nanoemulsions  
Microemulsions  
Nanofibers

Liposomes  filled with SLN  
Liposomes  filled with Nanoemulsions  
Nanoemulsions with SLN Shell  
Nanofibers containing Microemulsions or Nanoemulsions
Conclusions

• Bottom-up design of new complex structures leads to new functionalities

• Clear benefits in terms of functionality, solves old problems, but also generates new ones
  • Improved safety/quality and health benefits (bioactives)
  • Lifetime, mobility and location in food systems more complex

• Simple nanostructures as building blocks of more complex structures → Composites
  • Very difficult to predict what’s coming next – structures are build faster than new properties can be determined
  • This is rapidly blurring the boundary between nano and macro → underlying structures are nano (just like in biology), but the build system is macro