Utilization of Interfacial Engineering to Improve Food Emulsion Properties

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Traditional (Single-Step) Method of Emulsion Formation

1. Separate Oil and Water Phases
2. Emulsifier
3. Homogenization
4. Formation
5. Emulsion
6. Stabilization
Limitations of Single-Step Method

- Some emulsifiers are efficient at forming small droplets during homogenization, but not at providing good stability.
- Some emulsifiers provide good stability, but are inefficient at forming small droplets during homogenization.
- Existing emulsifiers provide limited scope for developing encapsulation & delivery systems.

Hypothesis: Can we develop a new emulsifier strategy that combines the fast adsorption of small molecules and the good stability of large polymers to create emulsions with improved performance and functionality?
Multi-Step Emulsion Formation

Separate Oil and Water Phases

Homogenize

Primary Emulsion

Add Biopolymer

Secondary Emulsion

Single-Layer

Two Layers

LbL

Pectin (wt%)
Control of Interfacial Characteristics

• Control of Interfacial Properties
  – Charge Sign and Density
  – Thickness
  – Packing & Permeability
  – Rheology
  – Responsiveness

• Control of Emulsion Properties
  – Stability, Rheology, Release
Potential Advantages of Multilayer Emulsions

• Improvement in Stability of Emulsions to Environmental Stresses
  – pH, Ionic Strength
  – Heating, Chilling, Freezing
  – Dehydration

• Encapsulation and Delivery of Functional Components
  – Protection of Labile Ingredients
  – Controlled or Triggered Release
Potential Disadvantages of Multilayer Emulsions

• More Difficult to Prepare
  – Prone to flocculation

• More Expensive to Prepare
  – Additional ingredients required
  – Additional processing required

Problem: Research is needed to establish optimum preparation conditions (ingredients and processes) for preparation of multilayer emulsions with specific performance and functionality.
Overall Project Objectives
Optimization & Application of Multilayer Technology

Food Ingredients
(Emulsifier, Biopolymers)

Preparation Conditions
(pH, I, T, Mixing)

Objective 1:
Prevent Flocculation

Interfacial Properties
(Charge, Thickness, Response)

Objective 2:
Control Interface

Emulsion Properties
(Stability, Rheology, Release)

Objective 3:
Create New or Improved Functionalities

Application
(New Food Products or Ingredients)
Understanding Formation of Multilayer Emulsions: Theoretical Model

$C_{SAT} = \text{Characteristic Saturation Concentration}$
- The minimum amount of polymer required to completely cover all of the droplet surfaces.

$C_{ADS} = \text{Characteristic Adsorption Concentration}$
- The minimum polymer concentration required to ensure adsorption occurs faster than collisions.

$C_{DEP} = \text{Characteristic Depletion Concentration}$
- The polymer concentration where depletion flocculation is first observed.
Theoretical Stability Map
Effect of Droplet & Polymer Concentration

For stable system: $C_{\text{Ads}} < C < C_{\text{Dep}}$
Multilayer Emulsion Formation:
Bridging & Depletion (pH 3.5)

Pectin Concentration

Coating Properties:
- Surface load ($\Gamma$)
- Thickness ($\delta$)
- Permeability
- Responsiveness

Droplet Concentration: 1 wt%
## Multilayer Emulsion Formation: Establishment of “Creaming Stability” Map

<table>
<thead>
<tr>
<th>pH &lt; pI</th>
<th>Droplet Concentration (wt %)</th>
<th>pH &gt; pI</th>
<th>Droplet Concentration (wt %)</th>
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<tr>
<td></td>
<td>0.5 1 3 5 8 10</td>
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<td>0.5 1 3 5 8 10</td>
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<tr>
<td>Pectin (wt %)</td>
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<td>Pectin (wt %)</td>
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<tr>
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<td>C</td>
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<td>pH &gt; pI</td>
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<tr>
<td>Bridging</td>
<td></td>
<td>Depletion</td>
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</tr>
</tbody>
</table>

**Legend:**
- S: Stable
- C: Creaming
Understanding Formation of Multilayer Emulsions: Experiments

Measure:
• Adsorption ($\zeta$-potential); Microstructure (Microscopy); Stability (Laser Diffraction, Creaming); Rheology (Shear rheometry)
Multilayer Emulsion Formation: 
Establishment of Adsorption Range

ζ-Potential Measurements Show Where Adsorption Occurs
Interfacial Characteristics:
Determination of Interfacial Properties

ζ-Potential
Dynamic Light Scattering

Interfacial Properties:
• Polymer Concentration
• Thickness
• Packing
• Charge

Protein-Pectin Multilayers: $\Gamma_{\text{Sat}} = 1.6 \text{ mg m}^{-2}$; $\delta = 45 \text{ nm}$; $\phi = 2\%$
Application of Technology: Improving Emulsion Stability

Motivation

• Multilayer technology could be used to improve the stability of many food emulsions to environmental stresses

Environmental Stresses

• pH, Ionic Strength
• Thermal processing, Chilling, Freezing
• Dehydration
Multilayer Emulsion Properties: Extension of pH Range

\[ \text{pH} \]

\[ \zeta\text{-Potential (mV)} \]

\[ \text{Diameter (nm)} \]

1° β-Lg
2° Pectin

Adsorption

Primary
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0
Secondary
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0
Multilayer Emulsion Properties: Extension of NaCl Stability Range

Origin of Stability:
- Reduction in VDW
- Increase in ES
- Increase in Steric

1° β-Lg
2° Pectin

pH 3.5
Multilayer Emulsion Properties:
Improvement of Thermal Stability

1º β-Lg
2º Pectin

pH 4
Multilayer Emulsion Properties: Improvement of Freeze-Thaw Stability

1º β-Lg
2º Carrageenan
3 º Gelatin

0% Sucrose

Freeze-Thaw Cycles

Diameter (μm)

1000
100
10
1
0.1

0 1 2 3

Thick Layer
Multilayer Emulsion Properties: Improvement of Dehydration Stability

Primary

Secondary

1º

2º
Multilayer Emulsion Properties: Improvement of Oxidative Stability

Graph showing the TBARS (mM) over Time (Days) with different concentrations of Fe²⁺.

- 1º
- 2º
- 3º

Fe²⁺
Current Status of Multilayer Emulsions

• Emulsions containing lipid droplets coated by nano-laminated layers can be prepared by a simple cost effective method using food ingredients.

• These emulsions have improved stability to environmental stresses, such as heating, freezing, drying, pH extremes, and high mineral contents.

• Future studies are needed to determine their suitability for use in real foods (encapsulation, controlled release, triggered release).
Future Work

- Investigate use of mixed biopolymers to form the outer interfacial layers (so can control charge and thickness).
- Investigate methods of cross-linking adsorbed layers so that they retain functionality over wider range of conditions.
- Investigate digestibility of multilayer emulsions.
- Investigate applications to real food systems, e.g., beverage emulsions.
Publications

• 5. Guzey D, McClements DJ. Formation, stability and properties of multilayer emulsions for application in the food industry. ADVANCES IN COLLOID AND INTERFACE SCIENCE 128: 227-248 DEC 23 2006