食品乳化物結構與功能性的關連 (Structure–function relationships in food emulsions: Improving food quality and sensory perception. *Food Structure 1: 104-126 (2014)*)

Abstract: Increasing consumer demand for higher quality, cheaper, more convenient, and healthier emulsion-based products means that the food industry must have a good understanding of the relationship between the structural and functional properties of food emulsions. This review article provides an overview of the relationship between the composition and structural organization of oil-in-water emulsions and their physicochemical (optical, rheological, and stability) and sensory (appearance, texture, flavor, and mouthfeel) properties. It also discusses recent advances in the design of structured emulsions with novel functional properties, such as multiple emulsions, filled-hydrogel particles, multilayer emulsions, microclusters, and air-filled emulsions.

1. *Introduction*

- Many food products contain two immiscible phases (typically oil and water) as part of the ingredients, and it is crucial to mix and stabilize them well in order to produce high quality, stable, and sensory appealing products. These two immiscible phases are often incorporated into food products as emulsions, which are formed by dispersing one phase into the other in the form of small droplets.
- A wide variety of food ingredients and products can be considered to consist either entirely or partially as emulsions, or have been in an emulsified state sometime during their production, e.g., beverages, butter, cheese, colorants, cream, desserts, flavors, ice cream, margarines, milk, salad dressings, sauces, soups, and yogurts.
- The emulsified components of these foods play important roles in determining their distinct functional attributes, such as appearance, texture, stability, and flavor.

- 傳統上，乳化分成oil-in-water (O/W)與water-in-oil (W/O) (圖一)。也可依照液滴大小分類：nanoemulsions (液滴半徑10-100 nm)、miniemulsions (液滴半徑100-1000 nm)、macroemulsions (液滴半徑1000 nm-1000 μm)；但實質上，三系統的臨界的物化性質並無明顯的差異。
- 提升功能性之結構更複雜的乳化：oil-in-water-in-water (O/W1/W2)與water-in-oil-in-water (W1/O/W2) 。

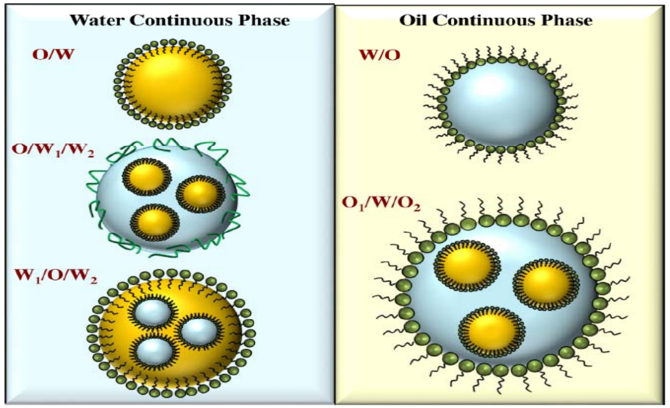


Fig. 1 – Schematic diagram of simple emulsions – oil-in-water (O/W) emulsion, and water-in-oil (W/O) emulsion, and multiple emulsions – oil-in-water-in-water (O/W/W) emulsion, water-in-oil-in-water (W/O/W) emulsion, and oil-in-waterinoil (O/W/O) emulsion.

- The various components within a food emulsion may significantly affect its bulk physicochemical properties and sensory attributes (Fig. 2).

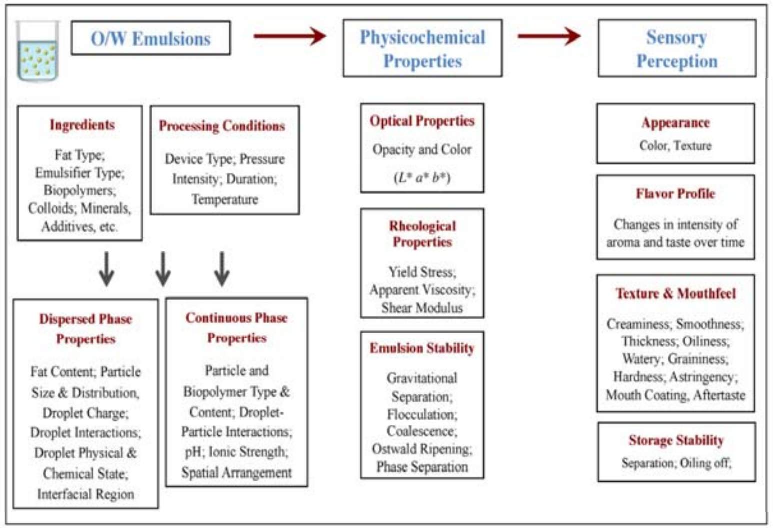


Fig. 2 – Overview of the relationship between oil-in-water emulsion properties and the bulk physicochemical properties and sensory characteristics of food emulsions.

2. Emulsion system formation

動力學上穩定的乳化是使用兩性化合物(amphiphilic compounds; 乳化劑 emulsifiers)來促進乳化形成與增進乳化穩定性而形成。當油滴 oil droplets 形成時，在油滴周圍乳化物形成薄膜，靠產生互斥力而防止油滴互相聚集。

乳化劑特性(種類與濃度)、bulk phase properties (介面張力及黏度) 及shearing conditions (壓力、次數及設備型式)會影響所形成油滴的特性(size, charge, interactions, and organization)，以及乳化物巨相的物化性質(rheology, appearance, flavor, and physical and chemical stability)。

常用的食品乳化劑包括低分子量介面活性劑、蛋白質、磷脂質、多醣類及其衍生物。

In addition to oil, water and emulsifier, most food emulsions also contain other ingredients to improve their texture, stability, and taste, such as thickeners, gelling agents, weighting agents, ripening inhibitors, flavors, and colorants.

3. Food emulsion building blocks

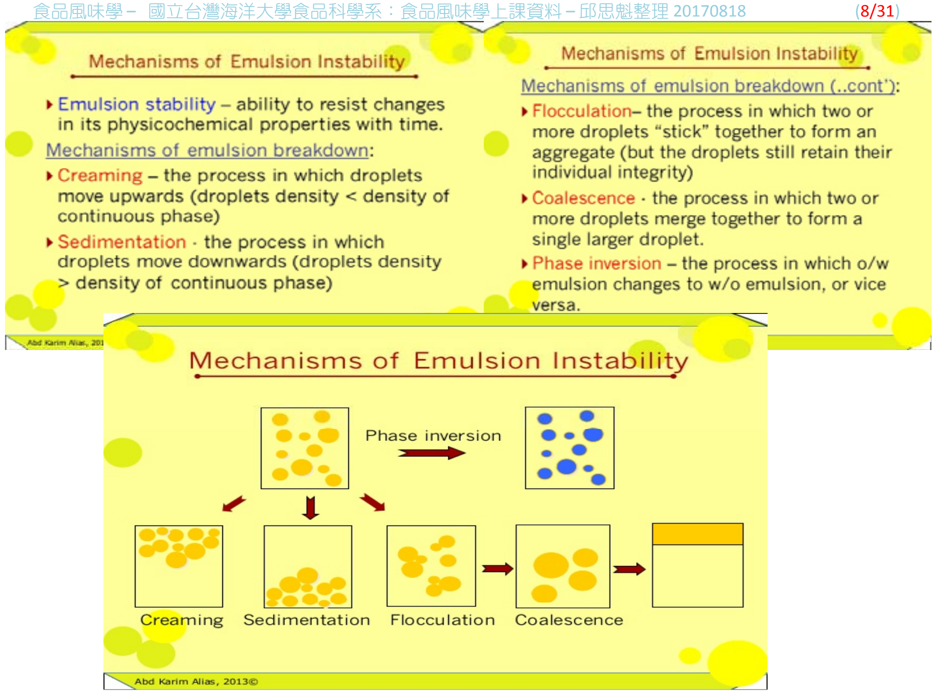
3.1. Dispersed phase 分散相

影響食品乳化系統之分散相的主要特性。

- Droplet concentration 液滴濃度。大大影響物化及感官性質，如光學的、流變的與感官的性質，液低濃度從飲料乳化物的數%至乳瑪琳的70%以上。
- Particle size distribution 顆粒大小分佈。乳化物中液滴的大小關鍵性地決定物化性質。平均液滴大小與顆粒大小的分佈可藉由加工條件(譬如均質機種類、壓力及/或時間，及溫度) 和/或 系統配方(譬如油、乳化劑、鹽類、醣類、共溶劑 cosolvents 和其它溶質) 的改變來控制。
- Droplet charge 液滴電荷。多數食品乳化物中液滴都帶有電荷，這取決於使用的乳化劑種類與溶液條件例如pH、離子強度及多價電解質。 液滴電荷主要影響液滴間的交互作用，油滴上電荷與所導致和周遭液滴及其它組成分間之交互作用會顯著影響食品乳化系統的物理的與化學的性質。

- Droplet interactions 液滴交互作用。Droplets in an emulsion may interact with each other and with other components through a variety of molecular and colloidal interactions, such as van der Waals, electrostatic, steric, depletion, hydrogen bonding, and/or hydrophobic interactions. 這些交互作用受到液滴特性(e.g., size, dielectric constant, and refractive index)、介面性質(e.g., charge, thickness, polarity, and packing)和連續相環境(e.g., dielectric constant, refractive index, pH, and ionic strength)的影響。

  取決於吸引和互斥交互作用的相對強度，油滴相互融合而合併(coalesce)、互相的絮凝(flocculate)或仍保持各自實體，這大大影響乳化的物化性質與穩定性。油滴也會同其它各種存在的組成分交互作用，譬如礦物質、蛋白質或多醣類。



3.2. Continuous phase 連續相

- 乳化為基底的食品產品的連續相，會包含各種的組成分如鹽類、醣類、酸類、鹼類、緩衝鹽類、澱粉顆粒、水膠體 hydrocolloids、顆粒物、氣泡和風味化合物。許多這些組成分會影響乳化物的結構(圖3)、物化性質及感官性質， 例如：澱粉顆粒、水膠體 及氣泡大大提高乳化物的黏度，並影響其它質地屬性。

3.3. Interfacial region 介面區域

- 介面區域含將油相與水相分隔的邊界層(圖1)，基本上此層包括乳化劑、油及水分子，和其它可能存在的組成分譬如礦物油、水膠體、抗氧化劑和促氧化劑等的混合物。
- 雖然介面區域在整個系統只占小的體積，其性質卻舉足輕重地影響食品產物的物化及感官性質，包括其流變性、穩定性與風味。

4. Sensory properties of food emulsion products

The composition and structural organization of emulsions ultimately determine their desirable sensory attributes. 故本節聚焦於乳化物的物化及感官性質如何受到分散相、連續相及介面區域等特性的影響 (Fig. 2) 。

4.1. Optical properties and appearance

- 乳化物主要的光學性質為 opacity (混濁或不透明度)及color。The overall appearance of emulsions depends on their composition and microstructure. The opacity and color of emulsions are mainly determined by particle concentration, size, and refractive index contrast, as well as the presence of any chromophores that absorb light.

4.1.1. Dispersed phase characteristics

- 乳化物的亮度 lightness 隨油的含量而增加，特別從0至5%油脂，此乃油滴的光散射增加(圖4)。這現象對低脂食品產品的研製可能有其重要意義，因降低亮度與不希望的乳脂感 creaminess 喪失有關連；因油滴濃度降低而致使低脂產品亮度也減少，可利用最適化配方及/或加工條件來彌補。

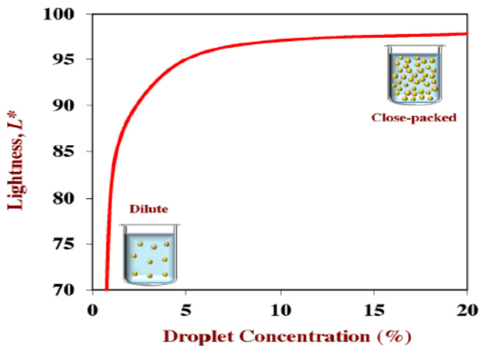


Fig. 4 – Dependence of the lightness of oil-in-water emulsions on droplet concentration.

4.1.2. Continuous phase characteristics

連續相中各種組成分由於散射或吸收光波的能力，能改變乳化物的光學性質。特別的物質譬如澱粉顆粒、蛋白質顆粒或氣泡，其作用幅度取決於相對折射指標 relative refractive indices 、濃度及顆粒大小。

- 加入散射光方式和油滴同樣的非油脂顆粒(譬如二氧化鈦)會提高乳化的不透明度，因而也是低脂產品的另一可能的替代。
- 連續相中水溶性色素的存在因選擇性吸收光波的能力，也會影響乳化。乳化的顏色受到溶解油相中任何發色團 chromophores 的影響。
- 加入會改變油滴的結構組織進而光散射樣式之成分也影響乳化為基礎的產品的外觀。例如刺槐豆膠加入乳化中會促進液滴凝集，故而降低亮度(圖5)。

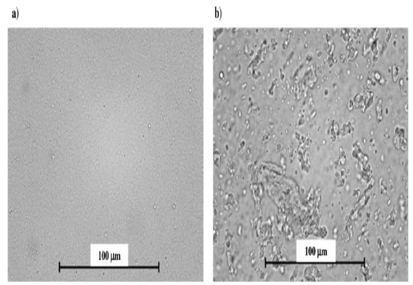


Fig. 5 – Optical micrographs (60×) of (a) oil-in-water emulsion (5% oil) and (b) mixed systems of locust bean gum (0.4%) and oil-in-water emulsion (5% oil).

4.1.3. Interfacial region

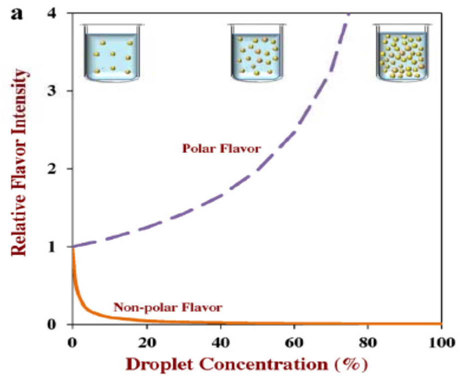
- 由於介面區域的厚度遠小於光的波長，不預期它對乳化物的光學性質會有大而直接的影響，且傳統乳化物中它的體積只占整個顆粒體積的一小部分；但在奈米乳化物，介面區域占有相當的比重因而其光學性質就重要。

4.2. Flavor profile

- 食品乳化物的整體風味輪廓 overall flavor profile 取決於存在各種相中的風味分子的分佈 (譬如油、水、介面、上部間隙)和攝食過程中它們的釋出樣式。從食品乳化物釋出風味分子，取決於它們的平衡分配係數與質量傳送動力學，風味釋出的特徵通常是在水相(滋味)或上部間隙(香氣)中風味分子濃度隨著時間而的增加 (flavor intensity– time relationship)。

4.2.1. Dispersed phase characteristics

- 乳化為基底食品的風味輪廓取決於各種油滴性質，譬如油種類、濃度、大小和物理狀態。不同來源的油與脂 (譬如玉米油、橄欖油、蔬菜油及動物脂) 所含的揮發性化合物濃度不同，故而貢獻食品的風味輪廓也不同。
- 油滴濃度影響揮發與非揮發風味化合物的感知，乃藉由改變彼等化合物分配partitioning 至油、水和上部間隙等相(圖6a)。



油脂含量的提高使得乳化物上部空隙的非揮發性風味減少，反之極性風味物質則增加。這現象對設計低脂產品尤其重要。

- The flavor intensity of full fat products may be characterized as balanced and sustainable throughout the course of consumption (‘‘sustained release’’), whereas in reduced fat products the flavor intensity may be unbalanced due to an initial spike (‘‘burst release’’) of flavor immediately after consumption, followed by low flavor intensity at later times (Fig. 6b).

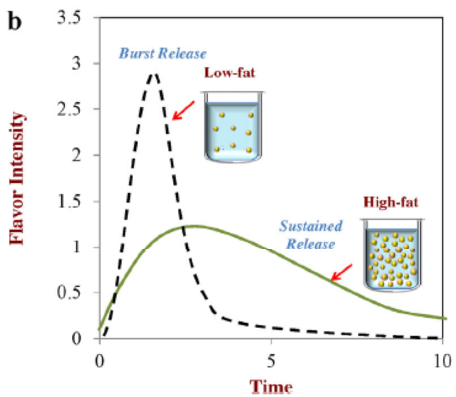


Fig. 6 – (a) Schematic representation of flavor dependence in oil-in-water emulsions on droplet concentration. (b) Schematic diagram of differences in flavor release profiles of low fat and high fat emulsion-based foods. A non-polar flavor molecule will give a ‘‘burst release’’ in a low-fat product, but a more ‘‘sustained release’’ in a high fat product.

- 低脂產品最初的風味爆出是由於水相中存在的非極性風味分子多於油相中，低脂產品的組成與結構因而須要重新設計，使得風味的釋出輪廓更相近於高脂產品。Sustained release may be achieved by encapsulating non-polar flavor molecules in delivery systems, such as filled hydrogel particles or microencapsulated particles.

- 圖7 ：油滴隨機分佈在慣用的O/W乳化物，在hydrogel 顆粒系統，油滴被嵌入水凝膠顆粒基質中。油滴被包封，這使風味釋出至上部空隙被延遲並持續。
- 油滴大小也影響非極性風味化合物釋出的動力學，因釋出進入水相及上部空隙之前，必須先從油滴擴散出來。

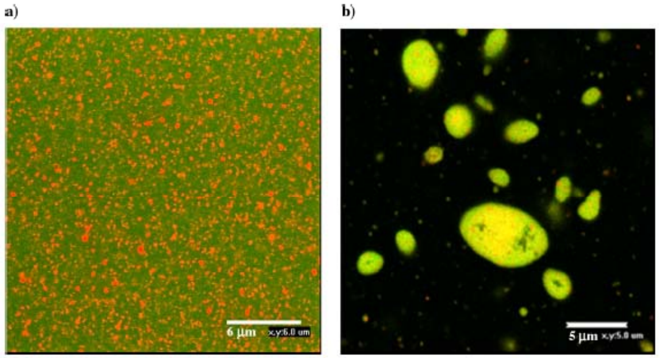


Fig. 7 – Confocal micrographs (60×) of (a) conventional oil-in-water emulsion (1%, w/w oil) stabilized by sodium caseinate (1%, w/w oil) (at pH 7) and (b) oil-filled hydrogel particles (1%, w/w oil) with sodium caseinate as the gel matrix and pectin as the continuous phase at pH 5.

4.2.2. Continuous phase characteristics

- 水溶液相內的非油脂顆粒及其它組成分，由於它們有改變揮發與非揮發分子的分配與質量傳送之能力，也會影響乳化為基底產品所感知的風味特性。濃稠劑與膠化劑能延遲風味分子擴散至舌上的滋味受體，故而影響整體風味輪廓。

4.2.3. Interfacial region

- The nature of the interfacial region may also influence the kinetics of flavor release. Some emulsifiers can bind flavor compounds and delay their release into the mouth and headspace. The nature of the interfacial region also determines how fat droplets behave within the mouth (e.g., their ability to stick to the tongue or to aggregate), which will alter the release of flavor molecules.

4.3. Texture and mouthfeel

- The ''texture'' and ''mouthfeel'' of emulsion-based food products plays an important role in determining their perceived flavor. A range of descriptors is commonly used to describe the texture and mouthfeel characteristics of food emulsions, such as ''creaminess'', ''richness'', ''smoothness'', ''sliminess'', ''thickness'', ''thinness'', ''watery'', ''firmness'', ''hardness'', and ''astringency'' .

4.3.1. Dispersed phase characteristics

- 在乳化為基底的食品，油滴的種類與濃度大大影響所感知的質地和口感。增加油滴的濃度，會提高''richness''、''creaminess''、''smoothness''、''thickness''、''fattiness''等的感知。

比較低脂與全脂版食品產品之間的差異，可用以說明油脂含量對質地與口感的影響。

- 在許多產品， 低脂版的 ''rich'', ''creamy'' 或 ''thick''的感覺不像對照之全脂版，部份歸因於黏度較低。
- 有些研究指出液滴大小影響食品乳化物的''creaminess''感。
- 增大乳瑪琳的油滴大小，所測摩擦值提高，關連roughness 粗糙性高 及creaminess 乳脂感低的參數。但也有報告指出油滴大小對乳脂感和thickness 的影響小。

這些不同的發現，顯示油脂以不同的方式影響不同食品的感官性質。

Droplet interactions: 液滴間的膠體交互作用colloidal interactions 對食品乳化產品的流變性與質地有顯著的影響。這些交互作用改變乳化物中分散相的有效體積分率，因而影響整體的黏度和質地性質。

液滴間的吸引力交互作用使液滴產生絮凝flocculation，由於連續相被困住絮狀結構內，這提高分散相的有效體積分率。誘使絮凝和所關連黏度的增加的方法包括：調整溶液pH或離子強度來降低靜電互斥力、添加生物聚合物來增加絮凝耗損或橋接吸引力、和加熱而提升球狀帶白質所佈層液滴之間的疏水性吸引力。

*Droplet size:*只有分散相體積分率較大$\Phi>0.45$時，乳化的液滴大小才對非絮凝型系統的黏度有一些影響。油滴的多重分散性(polydispersity) 也會影響乳化的黏度，因它影響有效堆積參數(effective packing parameter)。在多重分散乳化，液滴的堆積比在單一分散乳化更有效率，因小顆粒可納入大顆粒之間的空隙，故在相同的油脂含量下變成黏度較低。

4.3.2. Continuous phase characteristics

水相的性質也影響食品乳化物所感知的質地與口感。生物聚合物的存在，特別那些具有濃稠或膠化性質，改變乳化的質地與口感。乳化物的黏度直接和連續相的黏度成正比關

係，因而連續相中可提升黏度的任何組成份都將影響該系統的整體流變與質地性質。提高程度取決於存在組成分的濃度、構形及交互作用，以及整個系統的立體配列(圖3)。因而從低脂產品移除油滴而造成部分質地屬性的損失，可添加生物聚合物取代之。

4.3.3. Interfacial region

- 感知的乳化物質地與口感可透過調控油滴在口腔內的表現方式而改變，譬如是合併及/或散佈在舌上，這可透過改變乳化劑的性質來調控。研究顯示：在口中油滴傾向於合併，比起不合併者，具有較多乳脂口感與脂肪感。

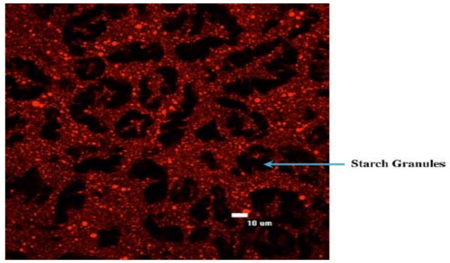


Fig. 3 – Confocal micrograph (60T) of mixed system containing 8% oil-in-water emulsion and 3.5% swollen starch granules (38 mm). The dark spots are starch granules (unstained) while the red spots are stained oil droplets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4.4 Food emulsion stability

Emulsions are thermodynamically unstable systems that are inclined to break down over time through a variety of physicochemical mechanisms.

4.4.1. Disperse phase characteristics

The structural and physicochemical characteristics of the disperse phase affect a number of different emulsion instability mechanisms，例如重力分離gravitational separation、絮凝flocculation、合併coalescence 和Ostwald ripening (圖8a)。

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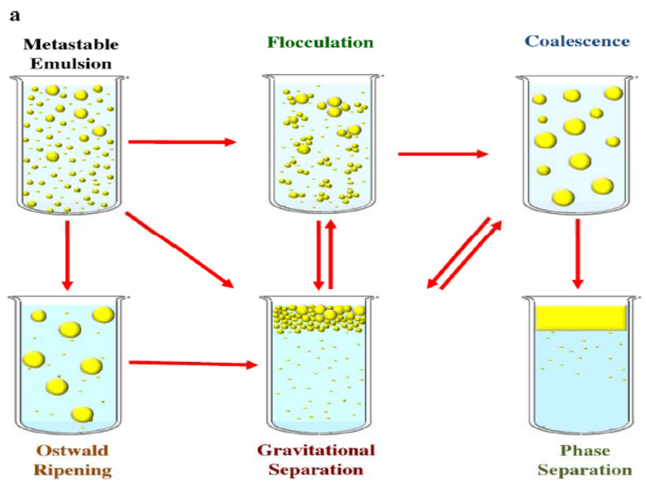
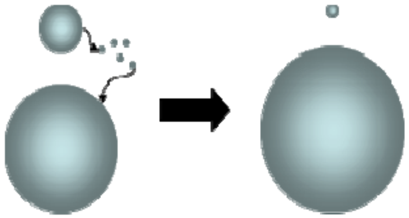


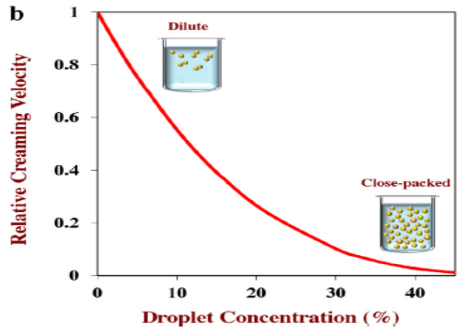
Fig. 8 – (a) Schematic diagram of most common instability mechanisms that occur in food emulsions: flocculation, coalescence, creaming, sedimentation, Ostwald ripening and phase separation. (b) Calculated dependence of the creaming velocity of the oil droplets in oil-in-water emulsions on droplet concentration.

＜補充＞ **Ostwald ripening** is an observed phenomenon in solid solutions or liquid sols that describes the change of an inhomogeneous structure over time, i.e., small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles.



- A **sol** is a colloidal suspension of very small solid particles in a continuous liquid medium. Sols are quite stable and show the Tyndall effect. Examples include blood, pigmented ink, cell fluids and paint. **溶膠**又稱**膠體溶液**，是在分散體系中保持固體物質不沉澱的膠體。Tyndall effect 指光被懸浮的膠體粒子（例如：乳劑、混懸劑）散射。

- 分散相密度影響重力分離發生的難易，乳化中液滴的濃度也會影響，濃度越高則 奶油化速率 creaming rate越慢(圖8b)。在大多數食品產品，提高液滴濃度並非抑止重力分離之可行的方法，但相同的機制(例如 hydrogel 顆粒) 改加入非油脂顆粒來抑制奶油化是可行的。液滴大小對重力分離也有重要的作用，奶油化速率隨顆粒直徑的平方而增加。故，延遲重力分離可採用降低液滴大小例如改變均質條件(提高密度或均質時間)與產品配方(例如乳化劑種類及濃度)等。



4.4.2. Continuous phase characteristics

The properties of the continuous phase may also influence a variety of different instability mechanisms in emulsions.

- 加入可提高連續相的黏度或膠強度的物質可阻止液滴的移動，譬如澱粉、膠類、糖類及/或蛋白質，因而，同時減少液滴的重力分離與聚集。
- 改變連續相的密度也影響重力分離的速率，變更圍繞油滴的水相的pH或離子強度會變更膠體交互作用 colloidal interactions 的幅度及範圍，故而對聚集的容易度。
- 加入非吸附性生物聚合物可減少絮凝，透過增加液滴間吸引力的耗損。另一方面，加入吸附性生物聚合物可經由架橋化 bridging機制而促進絮凝。

4.4.3. Interfacial region characteristics

The properties of the interfacial region surrounding the oil droplets in an emulsion often play a critical role in determining their stability. One of the most important effects is their impact on the colloidal interactions between droplets, i.e., their ability to modulate attractive or repulsion interactions.

- 介面區域厚度決定液滴間立體互斥力steric repulsion 的幅度與範圍。如果立體互斥力範圍大於任何吸引力譬如凡得瓦耳力或疏水性交互作用的範圍，絮凝就被抑制。
- 介面區域的電荷決定油滴間的靜電互斥力的幅度，可增加電荷的任何因素都傾向於增進穩定性。
- 介面區域的極性polarity 也會影響穩定性 － 介面層若親水性愈強，疏水性吸引力就愈弱，對聚集而言穩定性更高。

5. Instrumental assessment of food emulsion properties

A number of analytical methods have been developed to evaluate the sensory qualities of food products during product development. These instruments are useful for identifying the key factors that influence the sensory attributes of foods, and to provide quantitative information that may predict the sensory performance of foods. However, instrumental methods cannot model the extreme complexity of the human sensory system and hence cannot replace sensory analysis. Nonetheless, both instrumental analyses and sensory evaluations have their advantages and limitations.

- 5.1. Appearance
- 5.2. Aroma – volatile compounds
- 5.3. Taste – non-volatile compounds
- 5.4. Texture and mouthfeel
- 5.5. Microstructure analysis

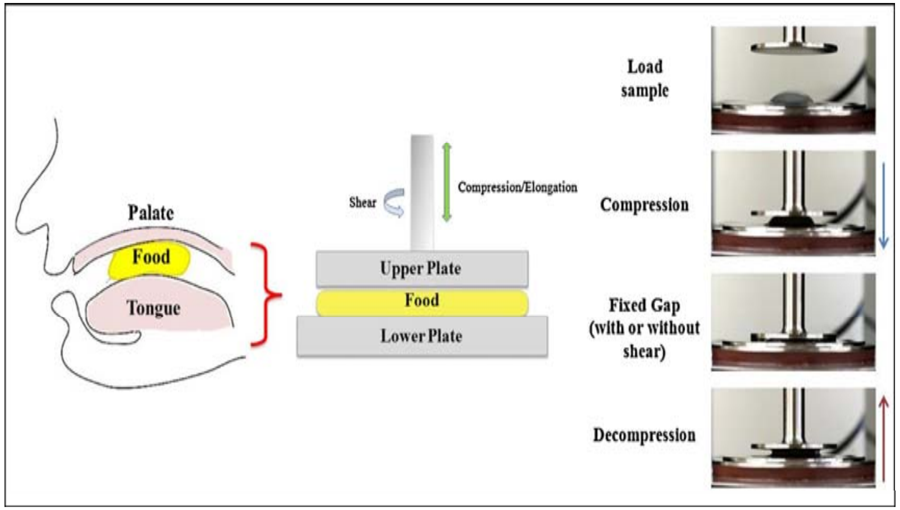


Fig. 9 – Schematic representations and photographic images of the instrumental mastication device designed to simulate the tongue and palate in the mouth.

6. Structural design approaches

Recently, there has been great interest in extending the functional performance of food emulsions using various structural design approaches.

6.1. Multiple emulsions
6.2. Filled hydrogel particles
6.3. Multilayer emulsions
6.4. Microclusters
6.5. Air-filled emulsions

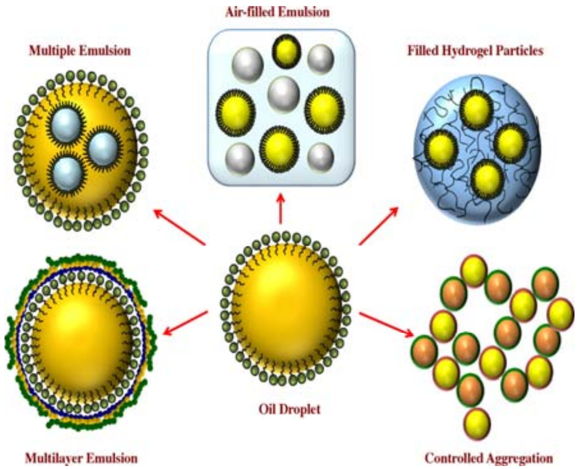


Fig. 10 – Examples of structured emulsions created by structural design principles using emulsion droplets as a building block.