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Self-assembly in food — A concept for structure formation inspired by Nature

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ABSTRACT

Structures present in Nature have evolved over millions of years to achieve optimized functionalities. In the recent past, characterization techniques have been developed progressively allowing to better access and understand complex bio-architectures and structure–function relationships. Since in Nature energy is limited, weak interactions play a fundamental role for building supramolecular hierarchical structures. Self-assembly formation is a crucial process for building those complex architectures. In this article we will describe what types of structures are formed in Nature using the self-assembly concepts, and how those can be utilized to generate new benefits in food products. Our description will concentrate on examples where both self-assembled structure formation and functionality in food products are conceived and enhanced on inspiration by Nature. Our major interest here concerns the following architectures: 1) cell membranes formed mainly by phospholipids, 2) the phospholipid/protein membrane of oil bodies and 3) self-assemblies formed during lipid digestion. We will then explain how these self-assemblies are used both in Nature and food material science to obtain compartmentalization and structures for improved product performance regarding controlled release of aromas and nutrients, bioavailability, Maillard-type chemical reactions and chemical and physical stability. Such self-assemblies are present in many food products but could be much better used to create new benefits for the consumer.

1. Introduction

Food products are made of bio-derived ingredients obtained from natural sources, for instance, plants, microbial organisms or animals. The used biomaterials have evolved over millions of years and their components such as lipids, proteins and carbohydrates form complex architectures like membranes, organelles, cells and organs. It is clear that the hierarchical structural organization of biomaterials can be directly linked to their unique properties and functions. In the present article we show how food scientists are inspired by naturally occurring structures for the design of tasty, healthy and nutritious products. Learning more about how Nature is controlling the functionality of such assemblies will allow to generate new purposes in food products creating new benefits for consumers.

The terms 'bio-inspired' and 'biomimetic' are often exploited to describe the use of a biological property or function. They describe very similar conceptions. Rawlings et al. [1] have made the following distinction: a biomimetic object must imitate and strictly copy something present in Nature while a bio-inspired product or process must only be influenced or informed by biology, making bio-inspired a much larger, general field. In processed food, strictly speaking, biomimetic is, to our knowledge, hardly used.

Cellular structures are fundamental building blocks of life and perhaps the most well-studied collection of complex systems that has inspired many scientific disciplines [2•]. One of the most important structural units of the cell architecture is the self-assembled arrangement of the cell membrane. As described recently by Whitesides, self-assembled structures are configurations that are much larger than those made by covalent synthesis [3••]. Membrane self-assembled structures are used in Nature for compartmentalization, i.e., controlling the transport, protection and chemical reaction pathway of molecules in the complex architecture.

Compared to other structuring approaches involving, for example, chemical reactions or high energy intake, self-assembly processes have the advantage to preserve the natural features of the used ingredients and biomaterials and to create structures similar to the one present in Nature.

Of particular interest for food scientists are the following naturally occurring self-assemblies: 1) phospholipid based membranes and their associated self-assembled structures; 2) monoglyceride self-assembled structures formed upon lipolytic digestion of fat globules in the digestion tract, and 3) phospholipid membranes containing proteins

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that stabilize oil droplets in plant and seeds (oil bodies). In the following chapters we will describe how phospholipid and monoglyceride self-assemblies can be used to generate new functionalities in food products, especially in terms of controlling the release and the bioavailability of nutrients, generating new flavor cocktails during Maillard type reactions, and modulating oxidation reactions. Finally, we will describe the main features of the naturally occurring oil bodies and give some examples on how these protein/lecithin membrane structures can be used in food products generating various benefits.

2. Lipid self-assemblies

2.1. Lipid self-assemblies in Nature

Cells are highly organized into functional compartments that are surrounded by membranes. It was proposed more than 80 years ago that the backbone of cell membranes is the structure of a bilayer made mainly out of phospholipids [4]. 35 years later, Singer and Nicholson proposed the 'fluid mosaic' model recognizing the liquid aspect of the lipid bilayer of the membranes, the high mobility of the components dissolved in the bilayers, and the role of proteins, glycolipids and cholesterol in the bilayers [5]. The bilayer membrane has several functions, often associated to compartmentalization, for example, to isolate the inside of the cell from the outside, to control the exchange of molecules between the compartments, to stabilize molecules and to prevent oxidative reactions [2•,6,7•]. These are all functions that food scientists also try to realize in relation to food and nutrition.

Bilayers are self-assembled structures. Self-assembly processes are common throughout Nature. 'Self-assembly' is not a formalized subject. It is actually used in literature to describe a wide range of different situations and processes ranging from the non-covalent association of organic molecules in solution to the growth of semiconductor quantum dots on solid substrates [8]. In the present article we limit ourselves to processes that involve pre-existing components and that are reversible and can be controlled by a proper design of the components (e.g. molecules). In this case self-assembly comprises a process by which an organized structure spontaneously forms from individual constituents as a result of specific and local interactions among the components. The information for structure formation is encrypted in the individual components [8]. If the elements are molecules, the process is termed 'molecular self-assembly'. In this concept the molecular structure is principally defining the final self-assembled arrangement and its properties. Furthermore, when the involved systems are at global or local equilibrium and do not dissipate energy, we are dealing with the so-called static self-assembly [8] (examples: bilayer formation, folding of globular proteins etc.). In case the formation of structure is occurring only if the system dissipates energy, we cope with dynamic self-assembly processes involving chemical reactions such as covalent bonding or hydrolysis [8]. The understanding of the latter form of self-assembly is still in its infancy [8–10]. We will concentrate here only on static self-assembly. Typical molecular interactions driving static self-assembly processes are van der Waals, hydrogen, electrostatic, or hydrophobic interactions allowing the lowering of the free energy of the system reaching a (local) minimum [2•].

In Fig. 1 we provide examples of self-assembled structures that can be found both in Nature and could be used in food products. The lipid bilayer in membranes is probably the best studied self-assembled structure that is present in Nature. Bilayers are the basic structural elements of lamellar liquid crystalline phases (Lα), vesicles or liposomes. The lipid bilayer is a planar thin polar membrane made of two layers of lipid amphiphilic molecules. In Nature, it keeps ions, proteins and other molecules where they are needed and prevents them from diffusing into areas where they should not be.

Biological membranes typically include several types of molecules other than phospholipids. A particularly important example in animal cells is cholesterol, which helps strengthen the bilayer and decreases its permeability. Cholesterol also helps to regulate the activity of certain integral membrane proteins. Membrane proteins have many vital functions. For example, they are involved in processes of cellular signaling [7•] and bilayer membrane fusion [12].

Beside planar bilayer structures, other self-assembly arrangements are present in Nature. They are called 'non-lamellar' self-assembly structures and built of curved lipid layers (have a non-zero curvature) deviating from a flat plane. The probably most commonly occurring non lamellar self-assembled structures are micelles. A normal micelle (or microemulsion droplet) is a self-assembled aggregate of surfactant molecules in which the hydrophilic "head" regions are in contact with the surrounding aqueous phase sequestering the hydrophobic single-tail regions in the micelle center (typical for structures with normal surfactant surface curvature). A reverse (or inverse) micelle or microemulsion droplet has the opposite structure, i.e., the hydrophobic tail region is in contact with the surrounding oil phase and the hydrophilic head region is in the interior of the self-assembly aggregate (typical for an inverse curvature). Micelles are the self-assemblies with the highest surface layer curvature.

Micelles, together with vesicles, have been recognized for some time now to be present in the small intestine and to play a central role in the digestion and absorption of fatty acids and lipophilic nutrients [13]. Vesicles are observed especially in the duodenum of subjects being fed with a triglyceride rich meal [13,14]. More recently, it was shown that during the course of enzymatic (Lipase) in-vitro digestion experiments of vegetable oils or human and cow milks several different self-assembled structures, e.g. an inverse microemulsion, inverse hexagonal (Hii), inverse micellar cubic and an inverse bicontinuous cubic phase (the three latter also denoted as non-lamellar liquid crystalline mesophases having an intermediate mean surfactant layer curvature), are formed and detected using small angle X-ray scattering (SAXS) and cryo-transmission electron microscopy (cryo-TEM) [15,16••,17,18]. These findings are supported by the known phase behavior of the oleic acid-monoglyceride-triglyceride-bile acid system at various pHs [19]. One main conclusion of these works is that the occurrence of different self-assembled structures during the lipolytic digestion of oil droplets significantly depends on the ratio between triglyceride and bile acids and on the pH [16••,19]. At low pH and low amounts of bile acids, the presence of self-assemblies having an inverse curvature is favored. An insufficient amount of bile salts can prevent proper dietary fat utilization and cause acid indigestion. The question, whether the symptoms related to, for instance, bile salt deficiency, can be directly linked to a difference in self-assembled structure formation during the lipolytic digestion of oil droplets, is still open.

Müllertz et al. tried to shed more light on the question whether self-assembled structures are also present in vivo [20]. Human intestinal fluids were collected near the ligament of Treitz (between the duodenum and jejunum). The authors showed evidence for structure formation, i.e., the appearance of non-digested oil droplets, vesicles and micelles, using atomic force microscopy (AFM) and cryo-TEM after the subjects were given a 'heterogeneous' liquid meal, which was rich in olive oil. However, other self-assembled structures were not detected, most probably because of lack of sensitivity of the used analytical tools. SAXS or cryo-electron tomography (CET) would bring additional information in this regard. Recently, it was shown that CET is a very powerful new method allowing to visualize self-assembly structural details that so far were not able to be observed with conventional tools. It enabled the direct visualization of the 2 independent water networks (Fig. 2, right) present in particles having an inverted bicontinuous cubic structure as well as the mechanism identification of particle stabilization of cubosomes [11••]. Note that non-normal micellar and non-vesicular self-assembled structures are very likely to be present in the part of the duodenum close to the stomach where pH is low and the ratio of lipid to bile acid is high.

In addition, the formed self-assembled structures serve also as a carrier and controlled release system of lipophilic nutrients in the gastro-