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Review

Utilizing unique properties of caseins and the casein micelle for delivery of sensitive food ingredients and bioactives

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ABSTRACT

Background: The use of biopolymers for the delivery of functional food ingredients and pharmaceuticals has increased dramatically. In this context a great attention has been paid to caseins and the casein micelle over the years, because of their superior functional qualities and nutritional properties.

Scope and approach: This review summarizes the unique properties of caseins and the casein micelle and how these properties enhance the successful delivery of sensitive food ingredients and bioactives. This information could be used as a baseline to enhance the capacity of casein and casein micelles in delivering biomolecules through better utilization of their unique properties.

Key findings and conclusions: Stability of caseins and the casein micelle during heating, freezing, and drying make them valuable in delivering food ingredients and bioactives. However, environmental modifications such as changes in pH perturb the stability of the casein micelle structure. Biological and physical functions of caseins are governed by their composition and flexible conformation. These unique carrying properties of caseins and the casein micelle and their physical and physicochemical changes in response to various environmental conditions such as heat, pH and high pressure can be successfully adapted in delivering functional food ingredients and bioactives in forms of micro-and nanocapsule, emulsions, hydrogels and edible films/coatings.

1. Introduction

Milk is a major component of human diet in many parts of the world. Beside the primary function in nourishing and providing immunological protection for neonates, due to its unique composition and properties, milk and its individual components serve as an important ingredient in the food industry. Some of these functions and properties are provided by milk proteins, which are usually grouped into two main fractions. A major fraction making up 80% of the total milk proteins is termed caseins and comprises proteins precipitating at pH 4.6. Individual caseins, including α_{s1}, α_{s2}, β and κ-casein, are unique proteins with respect to both their structure and function. They have open and flexible conformations and consist of hydrophilic and hydrophobic segments (Horne, 2002; Holt, Carver, Ecroyd, & Thorn, 2013; O'Mahony & Fox, 2013). Due to their highly hydrophobic nature, individual caseins are stabilized by the creation of a micellar structure (Bloomfield & Morr, 1973; Horne, 1986), which is chemically heterogeneous consisting of all four types of caseins and amorphous calcium phosphate. On a dry weight basis, the micelles consist of 94% protein and 6% small ions mainly calcium, phosphate, magnesium and citrate (Baumrucker, 2013; De Kruif & Holt, 2003; Fox, 2003). This structure, spherical in shape and commonly termed the casein micelle, varies in size from 50 to 300 nm and shows considerable variations in composition, structure and size distribution as well as in mineral composition (Ruettimann & Ladisch, 1987; Fox, 2003) under various conditions. Characteristics of individual caseins are given in Table 1.

Other than the micellar form, sodium or calcium salts of casein are widely used ingredients in the food industry where calcium and sodium caseinates are the two most frequently utilised. Caseins are mainly used as a protein ingredient in various food products to enhance their physical and functional properties, such as foaming, thickening, emulsification, texture, and most importantly to improve their nutritional levels. Caseins are Generally Regarded as Safe (GRAS status) and possess excellent binding capacity for ions

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Table 1
Comparison of individual caseins characteristics.

Characteristic	Type of Casein			
	α_{s1}	α_{s2}	β	κ
Native conformation	Open structure	Open structure	Open structure	Open structure
Quantity in milk (%)	1.2–1.5	0.3–0.4	0.9–1.1	0.3–0.4
No. of amino acid residues	199	207	209	169
Molecular weight	~23 000	~25 000	~24 000	~19 000
Location in milk at ambient temperature	Micelle	Micelle	Micelle	Micellar surface
No. of proline residues	17	10	34–35	20
No. of phosphate groups	8	10–13	5	1
No. of cysteine residues	0	2	0	2
No. of S-S groups	0	1	0	1
No. of S-H groups	0	0	0	0
Calculated charge at pH 6.6 (mV)	(−21)–(−23.5)	(−12.2)–(−17.1)	(−11.8)–(−13.8)	(−2.0)–(−3.0)

Adapted and modified from De Kruif & Holt, 2003; Sawyer, 2003; Brew, 2003.

and small molecules, exceptional surface-active and stabilizing properties, excellent emulsification and self-assembly properties and superb gelation and water binding capacity under defined conditions. Thus, due to important physical properties and behaviour, individual caseins and casein micelle appear as good candidates with appropriate carrier properties to deliver sensitive materials in food and pharmaceutical industries (Elzoghby, El-Fotoh, & Elgindy, 2011; Livney, 2010). For instance, the pH-responsive gel swelling behaviour renders caseins useful for programmable release of drugs or entrapped compounds. Caseins can also interact with other macromolecules to form complexes and conjugates with synergistic combinations of properties. Caseins possess ability in interacting with anionic or cationic biopolymers (non-covalent interactions). Additionally, caseins are characterized with various shielding and protective capabilities, essential for protecting sensitive payload, enabling to control bioaccessibility of the bioactive compounds and improve their bioavailability (Elzoghby et al., 2011; Livney, 2010; Singh, 2011; Wang, Wang, & Li, 2015). Further, the processing induced structural changes alter the physico-chemical properties and functionality of caseins and casein micelle (Considine, Patel, Anema, Singh, & Creamer, 2007; Huppertz, Grosman, Fox, & Kelly, 2004, 2008; Ye & Harte, 2014). Thus, not only the properties and functionalities of casein and casein micelles but also various processing conditions or some situations that take place in food processing can be employed to improve required properties enabling their wider applications in food and pharmaceutical products (Fig. 1). The present review summarizes the use of these unique properties of caseins and casein micelle in regards to delivery of sensitive food ingredients and bioactives, mainly focussing on capsules, emulsions, hydrogels and edible films as delivery systems.

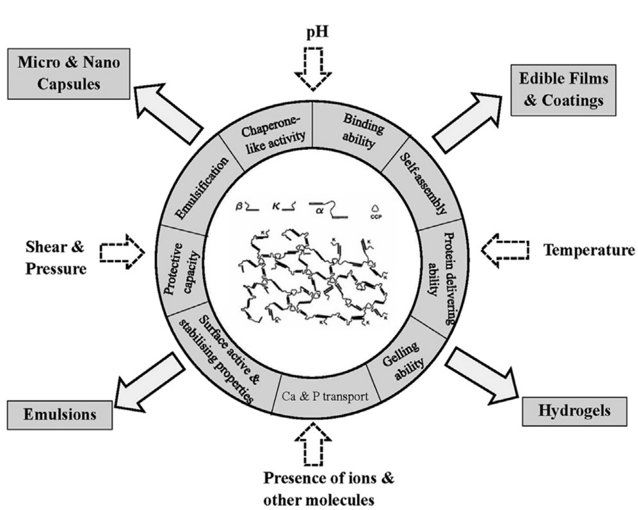

Fig. 1. Structural and functional properties of individual caseins and casein micelle relevant for delivering sensitive food ingredients and bioactives including major delivery systems and various processing conditions that can be employed to improve these properties. The casein structure is based on the model of Horne (1998).

2. Caseins and casein micelle based delivery systems

A wide variety of casein-based food and pharmaceutical delivery systems utilizing the properties and functions of casein and casein micelle have been described in forms of films (Bonnaillie, Zhang, Akkurt, Yam, & Tomasula, 2014), hydrogels (Song, Zhang, Shi, & Li, 2010; De Kruif, Anema, Zhu, Havea, & Coker, 2015), emulsions (Giroux, Robitaille, & Britten, 2016; Lesmes, Sandra, Decker, & McClements, 2010) and micro and nanoparticles (Bar-Zeev, Assaraf, & Livney, 2016; Jarunglumlert, Nakagawa, & Adachi, 2015; Semo, Kesselman, Danino, & Livney, 2007; Shapira, Assaraf, & Livney, 2010, 2012).

2.1. Micro and nanoparticles

Encapsulation is a process which entraps an active agent into a wall material producing particles on a nanometer (nano-encapsulation), micrometer (micro-encapsulation) or millimeter scale (Ray et al., 2016). Some recent applications of caseins and casein micelle in delivering sensitive food ingredients and bioactives in forms of micro and nanoparticles are summarised in Table 2. Individual caseins are an excellent wall/shell matrix for encapsulation because of their excellent emulsifying properties, low viscosity in solution, mild flavour, high nutritional value and protection against detrimental impact of processing, storage and gastrointestinal conditions (Jarunglumlert et al., 2015). High encapsulation efficacy of caseinate and micellar casein has been reported by many researchers (Ghasemi & Abbasi, 2014; Semo et al., 2007) and the structural characteristics of the casein micelle, especially its strong tendency for association and the high oxidative stability play a significant role in its encapsulation ability (Ghasemi & Abbasi, 2014; Zimet, Rosenberg, & Livney, 2011).

Caseins bind hydrophobic molecules via several mechanisms including hydrophobic interactions, van der Waals forces and hydrogen bonding (Livney, 2010). All caseins have blockwise distributed hydrophobic and hydrophilic regions derived from their primary structure of amino acid sequence (Fig. 2, Fox, 2003). The hydrophobic regions in casein provide binding sites to other hydrophobic molecules as interactions between hydrophobic regions are spontaneous. Vitamin D_2, a hydrophobic bioactive compound has been successfully encapsulated into the casein micelle through