NON-FOOD APPLICATIONS OF MILK COMPONENTS AND DAIRY CO-PRODUCTS: A REVIEW

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Abstract. *Milk contains a lot of different components with their own functional properties and some of them, such as casein, have been used in the manufacture of non-food technical products for many years. The present review deals with the non-food applications of (i) the major individual components of milk: proteins (casein; soluble proteins); lactose; milk fat and (ii) whey, a co-product of cheese and casein manufacture. New applications of milk proteins on a laboratory scale are focused on the manufacture of protein-based films and biomaterials. Also, fermentation of lactose and whey provides low molecular weight compounds and exopolysaccharides. These promising routes for giving added value to dairy co-products and effluents should be applied to achieving a great reduction in dairy industry wastes.*

INTRODUCTION

Milk and milk components are mostly used in foodstuffs in many different forms. Nevertheless, milk constituents also find numerous alternative applications in the non-food area such as in the manufacture of plastic materials, textile fibres, glues or in the production of ethanol or methane. Some of these technical applications have been well known for a long time, such as casein-based glues which were used in ancient Egypt, but novel uses are also proposed for opening new markets for components. Most of the technical applications are specific to one given milk component in relation to its structural and functional properties. Separation and extraction techniques may be of importance in the valorisation process of such individual components. Valuable components can be recovered by chemical and/or physical means in milk and dairy coproducts: casein is precipitated by adjusting pH to 4.6, whey proteins are recovered by ultrafiltration, lactose is concentrated and crystallised from whey. Besides, some applications concern the non-food uses of fractions containing different components together, which greatly simplify separation steps. This is the case for fermentation of dairy co-products such as whey converted to added value products.

MILK PROTEINS.

Casein and caseinates. Casein is the main protein (24–29 g·L–1) in bovine milk, as shown in Table I. In fact, casein of milk, involved in highly hydrated micelles, is based on four major components, αs1-casein (38%), αs2-casein (10%), β-casein

(36%) and κ-casein (13%) and a minor constituent, γ -CN (3%). Each constituent varies in amino acid composition, molecular weight (19 000–23 900), isoelectric point and hydrophilicity [72, 73].

Table I. Protein distribution in cow's milk.

Protein		Content in $g{\cdot}L^{-1}$	Relative proportion in %
Casein		25	100
	α-Casein	12	48
	β-Casein	9	36
	κ-Casein	3.25	13
	Minor constituents	0.75	3
Whey proteins		5.4	100
	β-lactoglobulin	2.70	50
	α-lactalbumin	1.20	22
	Immunoglobulin	0.25	5
	Serum-albumin	0.65	12
	Proteoses-peptones	0.60	10

Acid and rennet caseins are the two major types of casein available, depending on the coagulation process.

Non-food applications of milk components.

Acid casein refers to precipitated casein, obtained by adjusting skim milk pH to 4.6 with mineral acids such as hydrochloric or sulphuric acid. Lactic casein is precipitated by acidification due to lactic acid produced in situ with lactic acid bacteria designed as a starter. In rennet casein, coagulation is obtained by the action of chymosin (rennet), an enzyme which cleaves a chemical bond in κ-casein: the casein micelle is destabilised and forms a three-dimensional clot. Water-soluble caseinates can be obtained by solubilisation of caseins in alkali media such as sodium-, calcium-, potassium- or magnesium-hydroxyde, lime or borax. The commercially available sodium caseinate is obtained by dissolution of acid casein in sodium hydroxide at a pH close to 7. hange protein-protein interactions and proteins' interactions with their environment in order to control specific properties. Crosslinking agents are difunctional compounds which react with free reactive groups to make covalent linkage between protein chains, leading to the formation of a three-dimensional network. Crosslinked materials generally exhibit improved physical and mechanical properties. Considering these different properties, caseinate-based polymers can be used in several technical applications such as protective coating and foams, paper coating, adhesives or injection moulding disposables. The specific properties of casein relevant for technical applications are listed in Table II.

Casein as a coating or sizing agent. In such utilisations, casein acts as a binder for the coating material, generally a mixture of mineral materials, which is applied as a thin layer on the surface of the material. The hydrophobic/hydrophilic balance of casein increases its affinity for pigments, its ink-binding properties and its adhesion to various substrates. In the paper industry, casein is used as size for high quality glazed papers or for fine halftone illustrations. Water resistance can be achieved by exposure to formaldehyde vapours or by dipping in concentrated solutions of formaldehyde. Formaldehyde or dialdehyde are crosslinking agents which bind free amino groups to protein to give a threedimensional network. For example, wallpaper becomes water washable by adding a coating of casein solution brushed over with a solution of formaldehyde.

Table II. Principal technical applications of casein and caseinates.

Product	Property	Applications	Remarks/importance
Coating	Film forming ability Adhesion Technical properties	Paint	Still used in some paints
		Ink	Still used
		Paper	Still used
		Packaging	To be developed
		Leather finishing	Historical
		Textile coating	Historical
Adhesive	Good processability Bond strength Water resistance obtained by crosslinking	Water based glue	Historical Still used in some few applications
Plastic	Strength Good mechanical properties Water resistance obtained by crosslinking	Rigid plastic	Historical
		Disposable	Historical
		Fibre	Historical
		Coating Film/foil in packa-ging application	To be developed Laboratory scale
Surfactant	Surface tension Stability of interface	Emulsifier, detergent	Enhancement by chemical modification

extile industry. Casein was first employed in an way analogous to that of the paper industry: textile fabrics are impregnated with a casein solution and cross-linked either by formaldehyde vapours or by dipping into a solution of crosslinker.

Such casein coatings promote resistance to abrasion, enhance pigment binding and allow the textile to be impervious to moisture when hardened. Because of its film-forming and adhesive abilities, casein size also finds application in the textile industry.

Leather industry. Polyol plasticised casein [2] is used in the finishing operations in the leather industry combined with additional components such as acrylates [79], phenol derivatives, pigments for coloured products or binders such as gelatine or sulfonated castor oil [20]. The solution is coated on the leather before the surface is mechanically processed (brushed, ironed, glazed…).

Casein as a textile fibre. In 1935, Ferretti patented a process for casein textile called "Lannital®". An alkali-solution casein is spinned into a coagulation bath containing acid (sulphuric acid) and inorganic salts (aluminium and sodium salts). The spun fibres are insolubilised by dipping into a formaldehyde solution and water-washed. Casein fibres are known under trade names such as Aralac® (USA), Casolana® (Netherlands) and Fibrolane® (UK). Casein fibres resemble wool and were mostly used during the Second World War, generally combined with other artificial or natural fibres such as wool, cotton, viscose and rayon. Casein polymer fibres have also been grafted with acrylonitrile to give bicomponent fibres [14, 140]. Nowadays, commercial interest in casein fibres has declined, compared with more competitive synthetic fibres.

Casein-based packaging films and biomaterials. Transparency, biodegradability and good technical properties (barrier properties for apolar gases such as O2 and CO2) make casein films innovative materials for packaging. Nevertheless, casein-based materials have two major drawbacks in common with other protein-based biomaterials: limited mechanical properties and water sensitivity. To overcome weakness and brittleness, plasticisers are added to enhance workability, elasticity and flexibility. Plasticisers reduce intermolecular hydrogen bonding while increasing intermolecular spacing. By decreasing intermolecular forces, plasticisers cause an increase in material flexibility but also a decrease in barrier properties due to increasing free volume. To summarise, initially hard and brittle material becomes soft and flexible when plasticised enough.

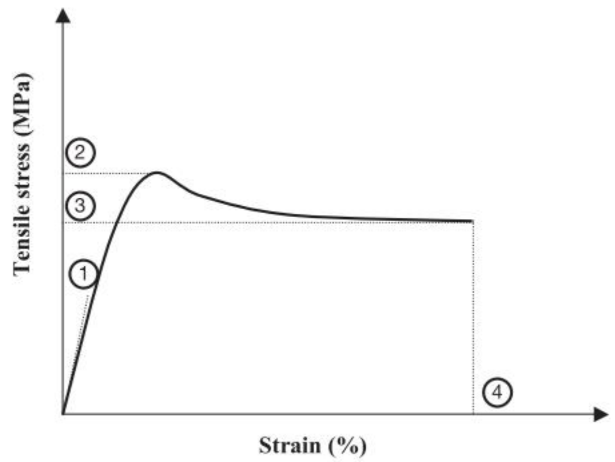

Figure 1. Typical stress-strain curve for caseinate-based films. ➀ Young's modulus; ➁ Tensile strength & stress at yield; ➂ Stress at break; ➃ Elongation at break.

Rigid casein plastics. Rigid plastic based on rennet casein is one of the best-known examples of nonfood application for milk protein. Rennet casein and fillers are mixed with 20–35% water before being mechanically processed by high pressure extrusion into plastic goods, which are cured for a period of several days in a dilute solution of formaldehyde. Any suitable pigment or colouring matter can be added. Casein plastic was first available in France and Germany under the trade name of “Galalith®” in the early twentieth century but other casein plastics have been patented under the trade names of Erinoid® (UK), Aladdinite® (USA), Casolith® (Netherlands), Lactoloid® (Japan) and Lactolithe® (France). The importance of casein plastics has now declined due to severe competition from synthetic plastics with better properties. Although casein plastics are still manufactured today into buttons, buckles and imitation-ivory knife handle, the range of articles is becoming more and more limited compared with the increasing number of articles made of synthetic plastics.

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