



## Rheological investigations of the interactions between starch and milk proteins in model dairy systems: A review

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### ARTICLE INFO

#### Article history:

Received 3 August 2010

Accepted 24 September 2010

#### Keywords:

Starch  
Amylose  
Amylopectin  
Milk  
Casein  
Whey protein  
Rheology  
Viscoelasticity  
Gelation

### ABSTRACT

This article reviews the interactions between milk proteins and starch, with an emphasis on the physico-chemical properties, particularly the rheological and microstructural behaviour of these systems. The dairy systems considered include model mixtures made of milk, individual milk proteins and milk protein ingredients, and model dairy-based food products such as acidified skim milk gels and processed cheeses. In addition theoretical modelling of milk protein–starch rheological systems are explored. Understanding how starches behave in model and applied systems will provide the dairy industry greater opportunities to produce new and difference products, at potentially lower costs. However, despite a large increase in the number of publications within this field, more study in the area is required to exploit the true potential of starch–milk protein interactions.

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## 1. Introduction

In systems in which milk proteins and starch co-exist, it is important to understand the mechanisms, interactions and synergistic effects that can provide maximum benefit to a food product. However, although starches and milk proteins, separately, have each been studied extensively, there is little in the literature on the interaction between milk protein and starch. In fact, only a few studies on the structure, gelatinisation, pasting, rheological properties and other physico-chemical properties of milk protein–starch mixtures have been carried out (Appelqvist & Debet, 1997). However, starches are becoming an increasingly popular addition to dairy systems because of their relatively low cost, availability and benefits. Studies investigating the interactions between milk proteins and starch or starch molecules (amylose and amylopectin) in solutions and in model dairy-based food products, such as processed cheeses and acidified milk gels, have recently been carried out.

This article reviews the latest developments in the general area of milk protein–starch interactions with an emphasis on the physico-chemical properties of these materials. Note that, as there are a large number of reviews on milk protein and on starch, these food ingredients are not reviewed here, but glossaries of the technical terms usually used for these ingredients are provided in Boxes 1 and 2.

## 2. Milk protein–starch interactions

### 2.1. Casein–starch interactions

The rheological properties of starch dispersions depend on the volume fraction occupied by the swollen starch granules. Doublier, Marzin, Visdeloup, and Lefebvre (1994) reported the effect of sodium caseinate addition on the behaviour of wheat, potato and tapioca starches. They showed a large decrease in the volume fraction occupied by swollen granules in the paste and in the concentration of starch macromolecules solubilised in the continuous phase. The addition of sodium caseinate resulted in a decrease in the swelling and solubility indices for all starches but had the

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### Box 1. Glossary — Milk proteins and dairy ingredients

**Caseins and casein micelles.** Casein, a mixture of several components, can be fractionated into four distinct groups:  $\alpha_{s1}$ -,  $\alpha_{s2}$ -,  $\beta$ - and  $\kappa$ -casein. The primary proteins exist as micelles made of the four types of casein. The exact structure of the casein micelle is not yet fully elucidated; however, it is proposed that the proteins are held together by hydrophobic interactions and by calcium phosphate bridges. At the surface of the casein micelle, a “hairy” layer made of  $\kappa$ -casein imparts a strong, repulsive, steric interaction that prevents casein micelle aggregation. Lowering the pH to pH 4.6, the isoelectric point of casein, diminishes the net electrostatic charge and repulsive steric interactions, resulting in the aggregation of the casein micelles and the formation of a protein network. It is this route that is used in the production of yoghurt. In practice, commercial yoghurts are obtained by the acidification of milk by bacterial cultures, which ferment lactose to lactic acid.

**Milk protein concentrate.** Milk protein concentrate is essentially skim milk with various amounts of lactose and the minerals remaining in the product. It is produced by passing the skim milk through an appropriate ultrafiltration membrane with or without diafiltration. The ultrafiltration step concentrates the casein and whey proteins without precipitation. Thus the casein in milk protein concentrate, like the casein in skim milk powder, still retains the micelle form found in milk (Mulvihill, 2003).

**Skim milk powder.** Skim milk powder is manufactured after the cream has been removed from whole milk by centrifugal separation. Then the skim milk is preheated and evaporated prior to spray or roller drying. Evaporation removes approximately 90% of the water from milk. Spray drying then further reduces the moisture content to 4% or less.

**Skim milk ultrafiltrate.** Skim milk ultrafiltrate is the mineral and serum component of skim milk. It consists of the milk serum components, mainly lactose and minerals.

**Sodium caseinate.** Sodium caseinate is obtained from whole milk, by destabilising the casein in milk by isoelectric precipitation. The insoluble casein is separated from the soluble whey proteins, lactose and salts, and a neutralisation with sodium hydroxide is performed prior to washing, to remove residual soluble solids, and spray drying.

**Whey proteins.** Whey proteins are the proteins that remain soluble after rennet or acid precipitation. The main whey proteins are  $\beta$ -lactoglobulin,  $\alpha$ -lactalbumin and bovine serum albumin.

**Whey protein concentrate.** Whey protein concentrates are dairy products enriched in whey proteins (60–85%) obtained from milk whey. The production procedures include different steps such as ultrafiltration/diafiltration and spray drying of the ultrafiltration retentate.

**Whey protein isolate.** Whey protein isolate primarily consists of whey proteins, but have higher protein contents (>90%) and proportionally lower concentrations of lactose and minerals than whey protein concentrates. The whey used for whey protein isolate manufacture is treated by ion-exchange chromatography, in which proteins are adsorbed on to an ion exchanger. It is then freed of salts by ultrafiltration before spray drying to yield whey protein isolate.

### Box 2. Glossary — Starch

**Starch.** Starch is the primary carbohydrate in plants. It is comprised of two polysaccharides, namely amylose and amylopectin. Both polysaccharides are comprised of  $\alpha$ -D-glucose connected by (1→4) linkages of short or long chains.

**Amylopectin.** Amylopectin is the major component of most starches. It is a much larger molecule than amylose, with a molecular weight of  $10^7$ – $10^9$  Da. It is a highly branched structure built from chains of  $\alpha$ -D-glucopyranosyl residues linked together mainly by  $\alpha$ -(1→4) and 5–6%  $\alpha$ -(1→6) linkages.

**Amylose.** Amylose is a heterogeneous mixture of molecules having variable molecular size and branching; the molecules are essentially linear polymers of (1→4)-linked  $\alpha$ -D-glucopyranosyl units with short (<0.1%)  $\alpha$ -(1→6) branches and have a molecular weight of approximately  $10^5$ – $10^6$  Da.

**Gelatinisation.** Gelatinisation is a swelling-driven process, which results in an irreversible order–disorder of the molecules within the starch granule, also observed as irreversible granule swelling, loss of birefringence, loss of crystallinity and leaching of amylose and/or amylopectin.

**Gelatinisation temperature.** The gelatinisation temperature is the temperature at which the starch granules begin to swell, lose crystallinity and show an increase in viscosity.

**Normal starch.** Normal starch can be divided into four main varieties: very low amylose (5–12% amylose), low amylose (12–20% amylose), intermediate amylose (20–25% amylose) and high amylose (25–33% amylose).

**Pasting.** When starch granules are heated in the presence of water up to the gelatinisation temperature, the granules lose their crystalline order and are able to absorb a large amount of water, resulting in swelling of the granules to several times their initial size (Eliasson & Gudmundsson, 2006). As the temperature increases further, the starch granules are disrupted, particularly when shear force is applied, which results in the formation of a starch paste. This starch paste consists of a continuous phase of solubilised amylose/amylopectin and a discontinuous phase of swollen starch granules/granule remnants, granule ghosts and fragments. When the majority of the granules have undergone disruption, the starch is said to be pasted.

**Peak viscosity.** The peak viscosity is attained when the largest percentage of the starch granules are fully swollen.

**Retrogradation.** Retrogradation occurs in the cooling phase as a result of the re-association of the starch chains to form an ordered structure after gelatinisation. A second peak in viscosity (set-back) occurs and the final three-dimensional network formed is an opaque gel.

**Starch granule.** Observed under polarised light microscopy, starch granules exhibit a birefringence cross (Maltese cross), which is a refraction of polarised light by the crystalline regions in the granules, as starch granules are composed of alternating semi-crystalline and amorphous growth rings. A starch granule is composed primarily of amylose and amylopectin. However, there are some minor components such as proteins and lipids, which are present at low levels.

**Waxy starch.** The starch grains of waxy starch consist only of amylopectin or very low levels of amylose (<5%). These starches are considered to be non-gelling starches and typically have a cohesive and gummy texture.

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