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Pectin meets protein –
a natural hybrid for food applications

1. Introduction
The application of pectins allows manufacturers of foods, pharmaceuticals, and cosmetics the specific modulation of textural, rheological, and organoleptic properties. Traditionally, pectins are widely accepted by consumers as a natural und green ingredient for the production of jams and marmalade. Major sources for the extraction of pectin are by-products from juice and oil manufacturing processes, typically including citrus peels and apple pomace. As such, the transformation of pectin from its *in situ* environment into a highly functional component is a multistep procedure involving various chemical, physical, and procedural treatments.

Commercially available pectins are typically utilized as thickening, stabilizing, and gelling agents for jams and fruit preparations in pastries and baked goods, yoghurt and dairy products, candy and confectionery products, as well as beverages. Herbstreith & Fox offers a wide variety of pectin types for numerous application fields. Interestingly, the combination of pectins with proteins derived from animal or more recently plant origins leads to hybrids with novel properties in terms of emulsifying and texturizing purposes, masking off-flavors or incorporating bioactive components – just to name a few. As such, the current application note highlights the general mechanism of pectin-protein complexation, their characterization methods, and some application fields to be used in foods.

2. The mechanism of particle formation
The underlying mechanism of pectin-protein particle formation is already well established and described in various scientific studies, papers, and patents [1]. In general, electrostatically charged biopolymers tend to attract or repel each other depending on the environmental conditions, which is schematically shown in Figure 1. The complexation of pectin and protein molecules is typically promoted such as that prevalent electrostatic forces are dominating which helps to induce the particle formation. In particular, acidic conditions are a major prerequisite to induce the complexation of oppositely charged proteins and pectins leading to the formation of so-called soluble complexes or precipitates – a fact which is also known as *„colloidal self-assembly“*. The pH-adjustment could be easily carried out by the utilization of organic or inorganic acids *(e.g. citric acid, lactic acid, sulfuric acid)* or by acid-producing bacteria.

Moreover, by modulating the biopolymer properties *(e.g. protein source, origin, pectin type, degree of esterification, biopolymer mixing ratio*) one could generate complexes with tailor-made characteristics in terms of size, charge, charge density, aspect ratio, and morphology for specific applications. In particular, the utilization of pectins having a low degree of esterification allows the formation of pectin-protein hybrids with particle sizes in the lower micron-range. Those particles are promising in the formation and stabilization of food emulsions, whereas complexes having particle dimensions ranging from 1 to 10 µm could potentially be used as fat replacer. In general, the manufacturing of biopolymer particles could be either sequentially or simultaneously realized. Subsequently after the complexation, the particles were thermally treated to generate highly concentrated or powdered products for various applications.

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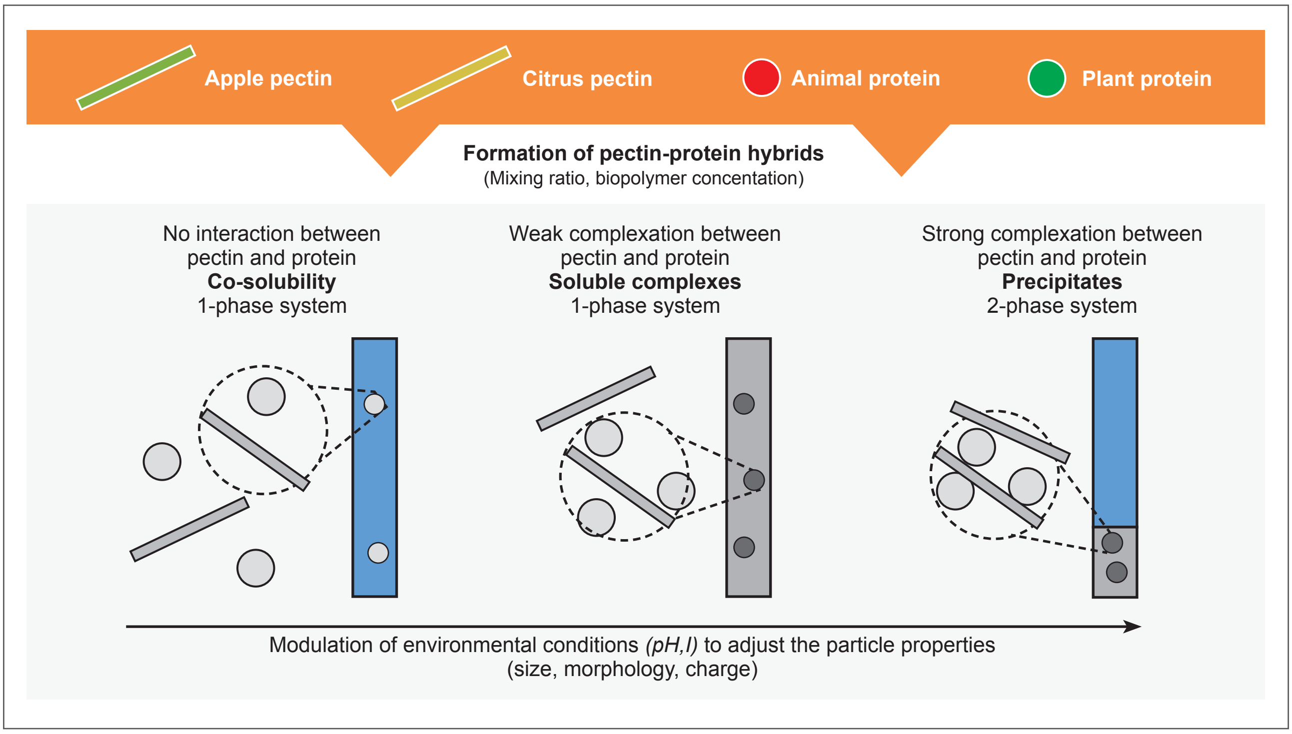

Figure 1. *The formation of pectin-protein-hybrids is based on electrostatic attraction forces that could be readily induced by changing environmental conditions (e.g. pH, temperature, ionic strength). The schematic representation highlights the interaction between pectin and protein as a function of pH.*

3. Analytical characterization

Technically, various physicochemical methods could be applied to characterize the pectin-protein hybrids as schematically shown in Figure 2. Microscopic and photospectrometric analysis are common tools to determine the particles` size and charge profiles. In particular, turbidity measurements as a function of pH are known as a simple and fast quality check in the laboratories. Moreover, dynamic and static light scattering equipments indicates both, the mean average particle sizes and the particle size distribution of a mixed biopolymer suspension. Light microscopy could be applied for pectin-protein hybrids with particle sizes >1 µm in order to determine their shape, morphology, and aspect ratio, respectively. Both, the particle concentration and pectin-protein ratio significantly contribute to the flow behavior and viscosity of the mixed suspensions, such as that rheological and tribological determinations are the methods of choice.

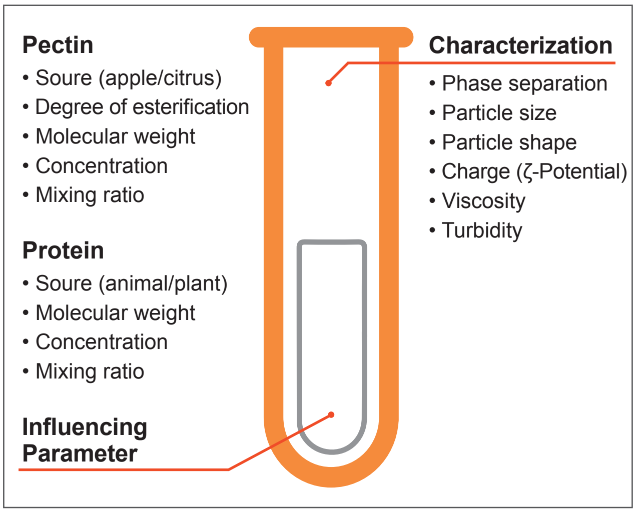

Figure 2. *Schematic representation of intrinsic parameters affecting the physicochemical properties of pectin-protein hybrids (e.g. size, charge, shape).*

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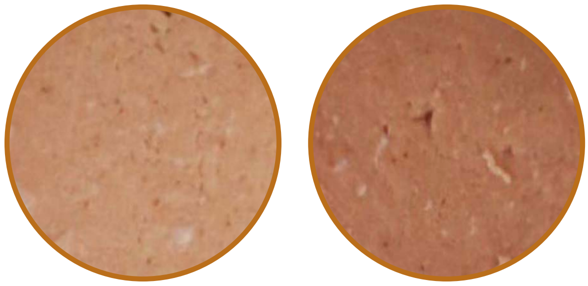
4. Some examples – a short overview

The practical utilization of electrostatic pectin-protein hybrids is various, as already demonstrated in numerous scientific studies. As such, it was shown that the complexes could be incorporated into food matrices as texture modifier, emulsifier, stabilizer, fat replacer, and gelling agents. More recently, the enrichment of micronutrients, the masking of bitter components, or the replacement of mammalian by plant proteins was introduced [1 – 3]. However, before being embedded into a food matrix, an initial hydration step of the single biopolymers is a major prerequisite. The pectin-protein hybrids are provided as spray-dried powders or highly concentrated liquids. The following section gives a detailed overview of some potential application fields for pectin-protein hybrids (*Figure 3*).

4.1. Fat reduction in meat products

Emulsion-type and raw-fermented sausages are two major groups of meat products with fat concentrations ranging between 30 to 70 % [4]. The fat incorporated significantly affects both, the texture and flavor of the final food product – a fact that highlights the sensorial acceptance by consumers. Some approaches have already investigated the impact of pectin-protein hybrids as potential fat replacer in meat products. In general, environmental conditions during the manufacturing process have to be chosen, such as that electrostatic complexes could be optimally embedded into the meat matrix. In particular, the incorporation of pectin-protein complexes with particles sizes > 1 µm in emulsion-type and raw-fermented sausages had no impact on the pH and water activity of the final product. More interestingly, spreadability, creaminess, and flavor sensation revealed unchanged after 50% of the fat was replaced by the pectin-protein particles [5].



Full fat control (40%) | **Fat reduced sample (20%)**

Fat replacement: "Raw-fermented sausage"

The application of pectin-protein hybrids in spreadable raw-fermented sausages was investigated. Pectin-protein ratio promotes the spreadability of the meat matrix.

Application scenarios

- Enrichment of micronutrients
- Masking of bitter components/off-flavor
- Novel emulsifier
- Texture modulation
- Fat replacer & substitution
- Modulation of oil and fat digestion
- Replacement of animal proteins

Figure 3. *Potential application fields of pectin-protein hybrids in foods (Data taken from [5]).*

4.2. Surface modulation in food emulsions

Foods, cosmetics, or pharmaceuticals are part of our daily life. These emulsion-based products mainly consist of an oily and watery phase which are *kinetically* stabilized over a certain period of time by a single or combined emulsifier system. Generally, synthetic or natural emulsifier and stabilizer are therefore utilized. In various scientific studies it was already proven that pectin-protein complexes have an excellent surface activity and emulsifying property in forming and stabilizing model oi-in-water emulsions [6]. Particularly, apple pectin-whey protein particles were utilized as emulsifier leading to oil-in-water emulsions with enhanced salt-, heat, and freeze-thaw stability. A simple mixing step already led to the formation of stable emulsions without utilizing expensive high pressure homogenizers.

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4.3. Masking of bitter components

Plant-based protein isolates or -hydrolysates are interesting ingredients for liquid, semi-solid, or solid foods due to their nutritional profile. Both, their functional and nutritional properties are mainly determined by the plant source as well as the extraction, purification, and isolation conditions chosen. Pea, potato, sunflower, pumpkin, lentil, and canola – just to name a few – have been nowadays introduced as potential protein sources. Interestingly, some plant-based isolates or hydrolysates are known to carry bitter off-notes – a fact that is based on an electrostatic and/or hydrophobic interaction between the bitter component and the human tongue [7]. As such, a promising route to reduce or retard the bitterness was the electrostatic complexation of plant proteins with pectins resulting in a positive sensorial perception. Previous studies in model beverages have shown that the bitterness score could be reduced by 50% regardless of the pectin used (apple or citrus origin) [8, 9]. In addition, the degree of esterification significantly affected the particle size of the pectin-protein hybrids generated helping to control the mouth feel of the biopolymer suspension. Further tailor-made pectins as counterparts could contribute to the visual and rheological or viscosity.

5. Conclusion and future aspects

Previous studies have demonstrated the great potential of pectin-protein hybrids for foods, cosmetics, and pharmaceuticals, whereas mostly animal proteins were used as counterparts during the complexation process. In terms of sustainability, future investigations and developments are focusing on the application of plant-based proteins incorporated into the hybrids. In addition, the specific modulation of pectins are promising routes to tailor the particles´ properties for texturizing, emulsifying, and encapsulating purposes.

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