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Pectin - plant protein systems and their application

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Abstract

The techno-functional properties of plant protein are often inferior to those of animal origin, mainly due to denaturation during extraction. They require improvement for easier incorporation into food products, and combinations with pectin were tested for this purpose. Coacervates, formed mainly by electrostatic interactions, and conjugates, formed by covalent binding, improved protein solubility around the isoelectric point, surface activity and emulsion and foam stability. Active (often hydrophobic) ingredients were encapsulated by conjugates or bilayers or within nanoparticles to stabilise them in a hydrophilic environment and to control their release. Coacervates were also able to mask the bitter taste of plant proteins by blocking electrostatic interactions with taste receptors, and fibrous compounds were prepared as meat replacers.

Pectins were well suitable for many combinations with plant proteins in food systems owing to their variety of properties resulting from botanical origin or modification. The impact of pectin structure on the different interactions, however, has been studied only to a limited extent, and not all results were convincing. Additional work, using well defined and characterised pectin samples, is required for a better understanding of the interactions, aimed at an extended plant protein application for human nutrition.

Contents

1. Introduction

The increasing demand of a growing world population for sustainable and high-nutritional food products enhanced the interest in the utilisation of plant proteins as food ingredients within the last decade (Sá et al., 2020). Proteins are a main component in different terrestrial plants such as legumes, grains, seeds, pseudocereals, almonds and nuts. The protein content may vary from about 10% in rice to about 45% in soy beans (Sá et al., 2020). Initially, protein concentrates and isolates were by-products of the extraction of oil (e.g. from soy and rapeseed) or starch (e.g. from corn, wheat and potato), but nowadays, the production of plant protein components for human consumption is a rapidly growing branch of the food industry (Sá et al., 2020; Ebert et al., 2020). Plant proteins are incorporated and often strongly bound within the plant cellular structure and require special extraction procedures. The production process for the isolation of plant proteins is, therefore, often more complicated than those of animal proteins from milk or egg. The processing parameters, such as pH, ionic strength, solvent type and extraction temperature, may considerably affect the quality of the extracted protein and cause at least partial denaturation. In particular, protein solubility is often reduced, which is a key factor for protein functionality (Li & de Vries, 2018; Ebert et al., 2020; Mota da Silva et al., 2021). The limited techno-functional properties may complicate the incorporation of plant proteins into food products, which is widely determined by the “interaction capacity” and depends in particular on protein conformation and surface properties. Techno-functional properties of plant proteins may be additionally affected by processing conditions during food production (Qamar et al., 2020).

Independent of the extraction process, isolated plant proteins are a mixture of different protein fractions with varying properties. For instance, protein products with a high share of prolamins and glutelins are less water-soluble than those containing mainly globulins and

albumins (Ebert et al., 2020). Moreover, the solubility of all proteins depends on the pH and is minimum at the isoelectric point (pI).

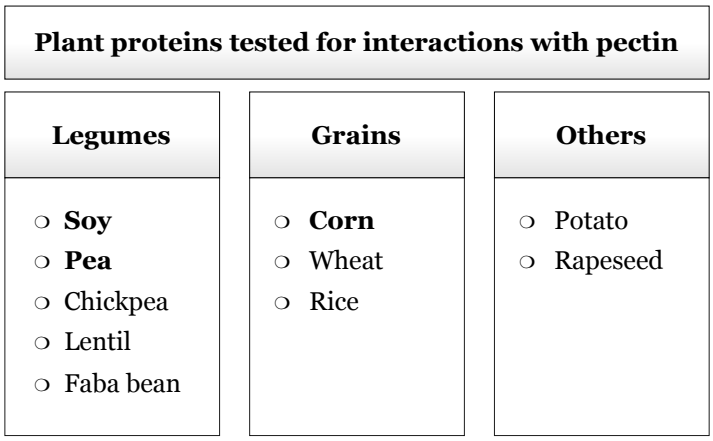

Fig. 1: Plant protein types studied for their interactions with pectin.

Soy, pea and corn protein were the most studied plant proteins with regard to their interactions with pectin (Fig. 1, Table 1). Soybeans contain about 40 - 45% protein, the main fractions are conglycinin and glycinin with together more than 80% (Nishinari et al., 2014). The proteins become denaturated during commercial extraction by heating steps. As a consequence, their solubility is strongly reduced and is minimum around pH 4 - 5, in the range of the pI. Pea proteins are contained in pea seeds with about 20% (Barać et al.,2015) and consist of two major fractions, a globulin fraction with 65 - 80% and an albumin fraction of 20 - 35% of the total protein content (Schroeder, 1982). The pI of pea protein isolates is around pH 4.5, and the solubility is low in this pH-range. Corn contains about 8% protein (Shukla & Cheryan, 2001), the main fractions are zein and glutelin, with each about 40%. Zein includes a high proportion of non-polar amino acids, this makes it hardly soluble in water below pH 11 but well soluble in aqueous solutions containing e.g. urea or anionic detergents or in apolar solvents like ethanol. The pI of zein is around pH 6. Another protein that should be mentioned here, though it was only seldom tested together with pectins, is from rapeseed (also named as canola). Napin (20%) and cruciferin (60%) are the main fractions of canola protein (Kristjansson et al., 2013; Wanasundara et al., 2016). Napin has a very high pI of about pH 9 - 11, and it is soluble in a range of pH 2 - 10. This high pI allows strong electrostatic interactions with pectin over a broader pH-range than with most plant proteins. Other plant proteins, which were investigated in combination with pectin were from legumes (chickpea, faba bean, lentils), grain (rice, wheat) and potato (Fig. 1, Table 1).

Table 1: Overview of the reviewed pectin-plant protein system with information about the pectin type and degree of methoxylation, protein type and tested pectin-protein system. HMP = high-methoxyl pectin, LMP = low-methoxyl pectin.

Plant protein	Pectin type	System	Authors	Year
Chickpea	HMP, citrus	Bilayer emulsion	Moser et al.	2020
Corn (zein)	HMP, citrus	Nanoparticles	Chang et al.	2017
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Chang et al.	2017
Corn (zein)	HMP, citrus	Nanoparticles, pickering emulsion	Chen et al.	2018
Corn (zein)	Pectic acid, ivy gourd	Nanoparticles, encapsulation	Dhanya et al.	2012
Corn (zein)	Pectic acid, ivy gourd	Nanoparticles, encapsulation	Dhanya et al.	2020
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Feng et al.	2020
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Hu et al.	2015
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Huang, Xiaoxia et al.	2016
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Huang, Xulin et al.	2017
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Huang, Xulin et al.	2019
Corn (zein)	HMP, apple	Nanoparticles, pickering emulsion	Jiang et al.	2019
Corn (zein)	LMP, citrus	Nanopartiacles	Liu et al.	2006
Corn (zein)	HMP, LMP , citrus / apple	Nanopartiacles	Mukhidinov et al.	2011
Corn (zein)	HMP, sugar-beet	Nanoparticles, pectin gel cover	Soltani et al.	2015
Corn (zein)	HMP, sugar-beet	Nanoparticles, pectin gel cover	Soltani et al.	2015
Corn (zein)	HMP, citrus	Nanoparticles, encapsulation	Veneranda et al.	2018
Corn (zein)	HMP, LMP	Nanoparticles, pickering emulsion	Zhang et al.	2021
Corn (zein)	HMP, citrus	Nanoparticles, pickering emulsion	Zhou, F.-Z. et al.	2018
Faba bean	LMP, citrus	Bilayer emulsion	Muschiolik et al.	1989
Lentil	LMP, citrus	Coacervate, nanoparticles, interface	Jarpa-Parra et al.	2016
Pea	HMP, citrus	Bilayer emulsion	Gharsallaoui et al.	2010
Pea	HMP, citrus	Encapsulation	Guo et al.	2020
Pea	HMP, citrus	Coacervate	Lan et al.	2018
Pea	HMP, LMP, citrus	Coacervate	Lan et al.	2020
Pea	HMP, sugar-beet	Coacervate	Lan et al.	2021
Pea	HMP, LMP, citrus	Coacervate	Pillai et al.	2019
Pea	HMP, LMP, citrus	Coacervate	Pillai et al.	2020
Pea	HMP, citrus	Conjugate, interface	Tamnak et al.	2016
Pea	HMP, citrus	Conjugate, interface	Tamnak et al.	2016
Pea	HMP, LMP, citrus / apple / sugar-beet	Coacervate	Warnakulasuriya et al.	2018
Pea	HMP, citrus	Coacervate	Wei et al.	2020
Pea	HMP, citrus	Cacervate, interface	Yi et al.	2020
Potato	HMP, sugar beet	Conjugate, interface	Li et al.	2021
Potato	HMP, LMP, citus / apple	Coacervate	Yavuz-Düzgün et al.	2020
Potato, pea	HMP, apple	Coacervate	Zeeb et al.	2018
Rapeseed (napin)	HMP, citrus	Coacervate	Amine et al.	2019
Rapeseed (napin)	HMP, LMP, citrus	Foam	Schmidt et al.	2010
Rice (glutelin)	HMP, citrus	Bilayer emulsion	Xu et al.	2017
Rice bran	HMP, citrus	Bilayer emulsion	Zang et al.	2019
Rice	HMP, citrus	Coacervate	Yang et al.	2019
Soy	HMP, citrus	Suspension	Dekkers et al.	2016

Table 1 continued

Plant protein	Pectin type	System	Authors	Year
Soy	HMP, citrus	Suspension	Dekkers et al.	2018
Soy	HMP, citrus	Coacervate	Giancone et al.	2009
Soy	HMP, citrus	Coacervate	Jaramillo et al.	2011
Soy	HMP, LMP, citrus	Coacervate	Lam et al.	2007
Soy	HMP, citrus	Coacervate	Lam et al.	2008
Soy	HMP, citrus	Coacervate, interface	Ma et al.	2019
Soy	HMP, citrus / apple	Conjugate	Ma et al.	2020
Soy	HMP, citrus / apple	Conjugate	Ma et al.	2020
Soy	LMP, citrus	Coacervate, encapsulation	Mendanha et al.	2009
Soy	HMP, citrus	Coacervate, encapsulation	Nori et al.	2011
Soy	HMP, citrus	Interface	Piazza et al.	2009
Soy	LMP, Premna microphylla turcz	Cold gelation	Zhou, F.-F. et al.	2020
Wheat (gliadin)	HMP, citrus	Bilayer emulsion	Qiu et al.	2015
Wheat (gluten)	HMP, LMP, citrus	Nanoparticles	Joye et al.	2015
Wheat (gluten)	HMP, citrus	Conjugate, interface	Wang et al.	2019

There is a chance of improving the limited techno-functionality of plant proteins in food systems by combining them with polysaccharides. In particular, the low solubility around the pI, insufficient interfacial properties in emulsions and foams as well as a restricted ability for the encapsulation of ingredients may be considerably enhanced. Different cationic, neutral or anionic polysaccharides have been already tested for this purpose, e.g. chitosan, gum arabic, carrageenan or alginate (Li & de Vries, 2018; Lan et al., 2018). Pectin was chosen as a polysaccharide partner, since different pectin types with various chemical structures, which may be isolated from various botanical sources or prepared by modification using special procedures, should allow a broad range of interactions with plant proteins.

Pectins are part of the primary cell walls of all plants. Commercial pectins are obtained mainly from waste materials of citrus fruits, apples and sugar beets, and these were also the dominating pectin types tested for combination with plant proteins. (Table 1). Structure and properties of pectin are described in detail by several authors (e.g. Thakur et al., 1997; Endress & Christensen, 2009). Pectin molecules consist of a backbone of galacturonic acid (GalA), interrupted by rhamnose with bound side chains of different neutral sugars. The carboxyl groups of the GalA molecules may be methylated, and the share of methylated GalA units determines the degree of methoxylation (DM). Pectins with at least 50% methylated GalA residues are named as high-methoxyl pectin (HMP) and with less than 50% as low-methoxyl pectin (LMP). The DM determines the net charge of a pectin molecule; the lower the DM, the more un-methylated “free” carboxyl groups are available and the higher is the net charge. These groups may be distributed along the backbone randomly or in blocks, depending on the method of pectin processing and on the DM. Their pattern, described by the degree of blockiness (DB), determines the charge density of the pectin molecule, since blocks of free

carboxyl groups cause a high local charge density (Sperber et al., 2009). The pectin net charge depends not only on the DM but also on the pH. Around pH 2.9, the pK_o value of poly-GalA, nearly no free carboxyl groups are dissociated, independent of their number or distribution along the backbone, and the net charge is close to 0. The dissociation increases with the pH, and at the pK_a value, which may vary in dependence on pectin type from pH 3.5 - 4.5, about 50% of the free carboxyl groups are dissociated (Michel et al., 1984; Racape et al., 1989; Ralet et al., 2001). Depending on botanical origin and modification procedure, further substituents on the pectin molecule may occur. Carboxyl groups may be amidated, and other parts of GalA can be acetylated. Sugar-beet pectin has special properties due to a bound protein component. Feruloyl groups may be linked to arabinose and galactose (Thibault, Renard, & Guillon, 2001). Altogether, pectin type and structure should have a considerable impact on the interactions with plant proteins. Dissociated free carboxyl groups may form electrostatic interactions, hydrophobic methoxyl or acetyl groups may participate in hydrophobic interactions, hydrophilic carboxyl, hydroxyl and amide groups may undergo hydrogen bonds, and the protein moiety in sugar-beet pectin may contribute to surface activity.

2. *Theoretical aspects of pectin – plant protein interactions*

The following parts shall give a summary of some basics for a better understanding of pectin - plant protein interactions.

2.1 Role of thermodynamic compatibility

Thermodynamic compatibility is crucial for the interactions of all proteins and polysaccharides, and, thus, also of plant proteins and pectins. Most plant proteins as well as pectins are hydrophilic, at least in a certain range of pH and ionic strength, and have been investigated in aqueous systems. Compatibility may result in co-solubility, complex formation or precipitation (Tolstoguzov, 2000; Braudo et al., 2001; Tolstoguzov, 2007). Nowadays, also the terms associative and segregative phase separation are used in combination with or instead of compatibility / incompatibility (Pathak et al., 2017; Weiss et al., 2019). Fig. 2 shall combine the different models.

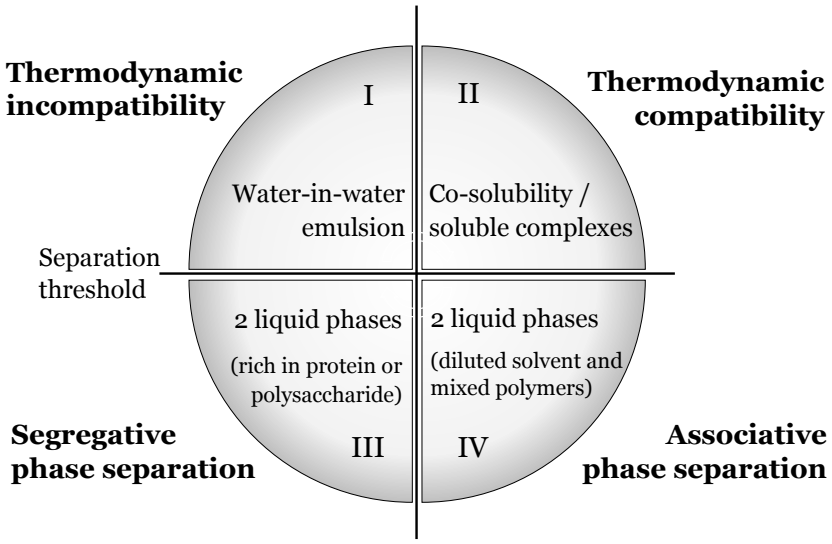

Fig. 2: Basic model for the phase behaviour of plant protein and pectin in watery solution.

Above the phase separation threshold, both components are contained in one phase. If the biopolymers are incompatible, mainly due to electrostatic repulsion, a protein-rich and a pectin-rich phase may form a kind of "water-in-water emulsion" (I). In case, the biopolymers are compatible, they are co-soluble or may interact and form complexes, for instance by weak electrostatic attraction (II). Phase separation is initiated for instance by an increase in concentration or mixing ratio of the biopolymers, by alterations of pH or ionic strength, or by gravity or centrifugation. After crossing the threshold, incompatible mixtures will separate into two liquid phases, one containing mainly the protein and the other the polysaccharide (III). This is named as segregative phase separation. Mixtures with compatible components may form two liquid phases (IV), an upper phase of diluted solvent and a lower phase

containing the soluble complexes. This is named as (liquid-liquid) associative phase separation. In the case of strong electrostatic attraction between the protein and the polysaccharide, mainly insoluble complexes may be formed (De Kruif et al., 2004), which afterwards may precipitate and sediment (not shown in Fig. 2). This process is also named as associative phase separation, but it is a liquid-solid type.

2.2 Types and mechanisms of interactions

Different physical or physico-chemical interactions as well as chemical reactions are possible between pectins and plant proteins. Extended information for the general understanding of types and mechanisms of interactions of proteins and polysaccharides give several excellent reviews. The structure of protein-polysaccharide complexes, the types of their interactions and the internal and external parameters were described for instance by Schmitt et al. (1998), de Kruif et al. (2004) Turgeon et al. (2007) or Schmitt & Turgeon (2011), and the modulation of protein-polysaccharide structures was reported in detail recently by Weiss et al. (2019).

According to the current knowledge, most interactions in pectin – plant protein systems are non-covalent. Electrostatic interactions, which mainly depend on the pH of the system, are dominating. In general, they may result from strong attraction between a positively charged protein and a negatively charged polysaccharide at pH < pI of the protein, from weak attractive interactions between uncharged or negatively charged proteins and positively charged polysaccharides at pH > pI as well as from the formation of local complexes between positively charged regions (“patches”) of the protein molecules and a negatively charged polysaccharide at pH > pI (Schmitt et al., 1998). Since pectin is a negatively charged anionic polysaccharide, the first and third type of electrostatic interaction are possible. The lower the DM of the pectin, the higher is the number of available free carboxyl groups and potential binding sites for the protein, and the higher the pH, the more of these groups are dissociated and charged. Electrostatic interactions are formed best in the pH range between the pI of the protein (mainly around pH 4 - 6) and the pK_o of the pectin at pH 2.9. An important parameter is also the pH of the electrical equivalence point (EEP), at which the number of positive charges of the protein and negative charges of the pectin in a defined system are equal. Electrostatic interactions are reduced by high ionic strength of the system, since ions may bind to the macromolecules. Hydrogen bonds between carboxyl and hydroxyl groups of pectin and protein as well as hydrophobic interactions between hydrophobic amino acid residues and methoxyl or acetyl groups of pectins may additionally stabilise the system. They are less dependent on pH but are affected by temperature. Higher temperature favours the hydrophobic interactions and lower temperature the hydrogen bonds. Non-covalent interactions are typical for the formation of coacervates and nanoparticles as well as for interactions at interfaces of emulsions and foams.

Covalent bonds between pectin and plant protein may be formed by a chemical reaction named as conjugation. This is a glycosylation (sometimes also named as glycation) process, based on a Maillard-type reaction. Free ε- or α-amino group of amino acid residues (lysine, histidine, tryptophane and arginine) of the plant protein and the carboxyl groups of the pectin backbone or reducing end-carbonyl groups of neutral sugar side-chains of pectin may undergo a condensation reaction (Oliver et al., 2006; de Oliveira et al., 2016). The glycosylation rate (also named as degree of graft) is strongly related to experimental settings (e.g. temperature, humidity, pH, time), to the polymer structures and to the ratio of protein and pectin, in particular to the relation between free amino groups and carbonyl groups (Oliveira et al., 2016). Conjugation is mainly performed in dried mixed systems by long-term heating at a defined relative humidity (dry-heating). The method was first described about 30 years ago by the group of Kato et al. (1990). Another method for the formation of covalent bonds between a protein and a polysaccharide component uses special linkers, like for instance cyanogen bromide (Kato et al., 1988) or laccase (Li et al., 2021). These reaction products are also referred to as conjugates. Conjugates were often applied in emulsions and foams to utilise the combination of the particular properties of the two components (Dickinson, 2009).

Fig. 3 gives a general overview of the studied pectin – plant protein systems included in this review.

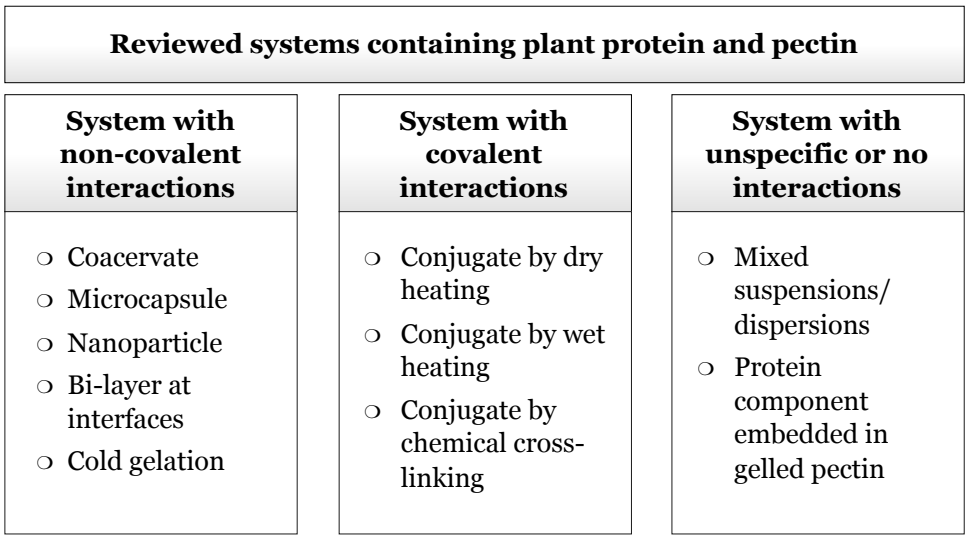

Fig. 3: Types of investigated systems containing pectin and plant protein.

3. *Studies of pectin - plant protein systems*

This review aims to give a general overview of the current knowledge in the field of pectin - plant protein interactions with a special focus on a possible impact of pectin type and structure. Different groups used many experimental setups and analyses and examined the effect of extrinsic factors such as pH, ionic strength, heating and energy input. Investigations in mixed solutions and dispersions covered the formation of coacervates, nanoparticles and conjugates. These combined systems were applied for an increasing solubility, interfacial stabilisation in emulsions and foams as well as for encapsulation of active ingredients. An overview of the reviewed papers gives Table 1.

3.1 Complex coacervates

When comparing existing research, the term "complex coacervation" needs careful consideration, since it has been used for different systems such as soluble complexes, insoluble complexes or layer-by-layer complexes (Moschakis & Biliaderis, 2017).

According to Comert & Dubin (2017), Eghbal & Choudhary (2018) and Amine et al. (2019), complex coacervation means the separation of a colloidal aqueous system into two liquid phases, one containing the two biopolymers and the other consisting mainly of the solvent. Schmitt & Turgeon (2011), Pathak et al. (2017), Kayitmazer (2017) and Timilsena et al. (2019) describe complex coacervation similarly as an associative phase separation with a liquid phase of biopolymers with higher density below a polymer-poor solvent supernatant. Both definitions agree with the system (IV) in Figure 2.

All interactions in complex coacervates are non-covalent. Beside dominating electrostatic interactions, hydrogen bonds and hydrophobic interactions may contribute (Kayitmazer, 2017; Pathak et al., 2017). Type and intensity on the one hand depend on the chemical structure of the involved macromolecules (amino acid composition, molecular weight, biopolymer flexibility, polydispersity, net charge, charge density, hydrophobicity) as well as on the total biopolymer concentration and the protein - polysaccharide ratio. On the other hand, solvent characteristics (solvent type, pH, ionic strength, co-solutes) and environmental factors (temperature, technological operations) are crucial (McClements, 2006; Schmitt & Turgeon (2011).

Interaction of complex coacervation is often investigated by measuring the turbidity of a protein – polysaccharide mixed system. Turbidity results from the formation of soluble complexes, which may undergo liquid-liquid phase separation, corresponding to (II) and (IV) in the model of Figure 2. This coacervate turbidity should be, however, carefully discriminated from that resulting from an aggregative liquid-solid phase separation (also named as

precipitation, aggregation or flocculation) as described above. Both mechanisms are often named similarly and may be identified for instance by microscopy (Amine et al., 2019).

Early studies on complex coacervation of plant proteins with pectin were performed using soy protein. Lam et al. (2007) prepared complexes by mixing soy protein isolate and citrus pectin with various DM between 71 and 32% at pH 3.8 (below pI of soy protein at 4 - 5 but above pK_a of the pectin around 3.5) in order to stabilise acidified beverages. Though LMP had a higher total net charge, it interacted less efficiently with the protein than HMP; the authors assumed electrostatic repulsion between unbound and bound pectin above a certain level of association. The HMP with lower net charge did not show this behaviour. A following work of this group (Lam et al., 2008) investigated the effect of pectin concentration using HMP and soy protein fractions at pH 3.8. A small amount of pectin caused bridging flocculation and destabilisation, whereas a sufficient amount improved the stability. Giancone et al. (2009) tested the interaction of soy flour with HMP at pH 4.6 below the soy protein pI in order to prevent instable insoluble protein complexes during film formation. The turbidity of the protein solution decreased and the solubility increased, probably due to electrostatic complex formation with pectin. Also Jaramillo et al. (2011) combined soy protein with pectin in a pH-range from 3 - 7 in order to increase the protein solubility around the protein pI at pH 4 - 5. Negatively charged soluble complexes were formed at pH 4 and 5, and the resulting repulsion increased the solubility. Solubility was, however, reduced at higher and lower pH, possibly due to a depletion mechanism. Ma et al. (2019) prepared blends of soy protein isolate and citrus pectin and adjusted the pH to 3 - 4.5 in order to form complexes of both components. They intensified the coacervate formation via electrostatic interactions by an ultrasound treatment interaction and improved the protein solubility in this pH-range.

Several works combined pea protein and pectin, and most of them evaluated the interactions by turbidity measurements. The first work (Gharsallaoui et al., 2010) tested the interaction between pea protein isolate and HMP at different pH and found increasing turbidity with decreasing pH due to the formation of soluble coacervate and of insoluble complexes by electrostatic interactions.

A series of works from one group tested coacervation of pea protein with pectin within the last 2 years. The first work used several commercial pectins and aimed to investigate the impact of pectin DM and DB (Warnakulasuriya et al., 2018). The authors found stronger interactions with pectin of high DM and with those with a more block-wise distribution of the free carboxyl groups. There remain, however, several questions. The tested pectin samples varied not only in the number (DM) and pattern of free carboxyl groups (DB) but also in their botanical origin from citrus, apple and sugar-beet. In particular, the sugar-beet pectin with its protein moiety is hardly comparable with the citrus and apple pectin. Moreover, there were strong unexplained differences in the values of galacturonic acid content. The following works of the

group used pectin sample sets which were prepared by modification in a controlled way in their lab. Pillai et al. (2019) studied the impact of the DM after alkaline demethoxylation as well as of the mixing ratio of protein and pectin. They found soluble as well as insoluble complexes of pea protein and pectin, and the interactions with LMP were described as stronger than those with HMP. This was explained by "an overall increased charge density" and by higher stiffness and rigidity of the LMP. Since the pectin was demethoxylated with an alkaline procedure, the resulting free carboxyl groups were randomly distributed. As a consequence, the total net charge increased but the charge density was probably not affected. Possibly, the authors mixed up "net charge" (depending on DM) and "charge density" (depending on distribution of free carboxyl groups). In this case, stronger interactions with LMP might indicate an impact of the higher net charge. Moreover, also in this work the strongly increasing galacturonic acid content of the pectin samples with decreasing DM was not explained. Since the same method was used for the determination of GalA as in the previous paper (Warnakulasuriya et al., 2018), a methodical problem cannot be excluded. It seems that the sum of DM and the content of GalA for every pectin in this work was about 100%, what is nearly impossible. In a following work (Pillai et al., 2020), the pectins were demethoxylated by a plant pectin methyl esterase. This enzymatic demethoxylation produces blocks of free carboxyl groups in the pectins. The prepared samples probably differed not only in their DM and total net charge but also in the DB and, thus, the charge density. Unfortunately, the latter parameter was not determined or discussed in this work. The pea protein solubility was increased by complex formation with pectin of high or medium DM but decreased using pectin of lower DM. The results are in contradiction to their previous work (Pillai et al., 2019) using alkaline demethoxylation. The authors assumed that the high charge density of the LMP reduced the complex formation but gave no further explanation on the role of the DB. A more detailed comparison of the results of both papers might have been useful for a better understanding of the separate impact of net charge (DM) and charge density (DB). Though the works of this group aimed to investigate the impact of pectin DM and DB on the interactions with pea protein, the results and conclusions are not completely convincing.

Other groups recently studied the coacervate formation of pea protein and pectin, too. Lan et al. (2018) intended to form soluble complexes in order to improve the limited solubility of pea protein in beverages. They determined critical pH values of coacervation from the turbidity curve in diluted solutions, and they applied a phase diagram, based on visual observation, for studying concentrated solutions with a too high initial turbidity. In a following work (Lan et al., 2020a) they tested the impact of the pectin DM using two commercial citrus pectin samples of DM 81 and 35%, respectively. They found that LMP showed initial interaction at lower pH than HMP due to the higher "overall charge density". Once more is not clear, whether this means higher net charge or charge density. The commercial pectin samples had, moreover, relatively low contents of GalA, since they contained other sugars for standardisation and were

not purified before using them. An additional effect of these ingredients cannot be excluded. Wei et al. (2020) studied the interaction of pea protein with various polysaccharides, including HMP, at pH around 7 and 3.5 in order to improve the stability of pea protein dispersions. They found an improved solubility by all polysaccharides and ascribed the effect of the HMP mainly to steric hindrance inhibiting pea protein precipitation. Also the solubility of hydrophobic rice protein (glutelin) should be improved by interactions with different polysaccharides, including HMP (Yang et al., 2019). A mixture of pectin and carboxymethylcellulose (CMC) was added to the suspended rice protein, the pH was set to 12 for 2 h, reduced to 7 and the mixture was dialysed. It was assumed that the rice protein was unfolding at pH 12, and that the following pH reduction allowed a co-folding of the protein after interaction with the pectin and the CMC in a ternary system. The resulting complexes were more hydrophilic than the initial protein and increased the protein solubility.

Interactions of HMP with napin, the plant protein with the very high pI of 9 - 11 from rapeseed, have been studied recently (Amine et al., 2019). The work examined in particular the liquid-liquid (coacervate) and liquid-solid (precipitate) associative phase separation by turbidity measurement in the pH-range from 3 to 11, with an increase in the negative charge of pectin and a decrease of the positive charge of the napin. Maximum turbidity was found at pH 4, the pH of electrical equivalence of the two components, which allowed the maximum formation of electrostatic complexes. At low pH, the interactions were strong and liquid-solid phase separation was dominating. At higher pH, the attraction was weaker and the phase separation was mainly liquid-liquid. It was also found that solid-like structures over time may rearrange and form liquid-like structures.

Some extracted plant proteins have not only a limited techno-functionality but also a bitter taste. It was postulated that this might result from electrostatic interactions of the protein with taste receptors in the mouth, and it was tested, whether electrostatic binding of the plant protein to pectin might block some of these interactions. In two recent studies, pea protein as well as potato protein solutions were mixed with pectin solutions at pH 3. In a first work (Zeeb et al., 2018), the impact the concentration of an apple HMP on pea and potato protein was tested. It was found that at low and intermediate concentration neutral protein-pectin complexes were formed, which rapidly precipitated but reduced the bitterness. This was, however, not a coacervation but a liquid-solid phase separation. Above a critical pectin concentration, the complexes were negatively charged and soluble, and the bitterness was considerably reduced, too. There was observed, however, also an increase in viscosity that might be critical for some applications. In a second work (Yavuz-Düzgün et al., 2020), only potato protein was tested but the pectin component was varied with respect to DM and botanical origin. The lowest bitter taste was found for the complexes with the highest negative

net charge (LMP), and citrus pectin was better suitable than apple pectin. However, HMP formed less viscous solutions that were easier to process.

Coacervates of plant protein and pectin were tested for encapsulation of components for their protection or controlled release. Encapsulation means the inclusion of an active component core within a stabilising shell in order to protect it and / or to release it in a controlled way (Moschakis & Biliaderis, 2017; Timilsena et al., 2019).

Guo et al. (2020) formed ternary complexes of hydrophilic pea protein and HMP and different surfactants, which were loaded with resveratrol, and studied its controlled release. The complexes were stabilised by electrostatic and hydrophobic interactions and / or hydrogen bond between the components, depending on the type of applied surfactant. The degradation of resveratrol and the in vitro digestion were retarded. There is, however, the question of a separate impact of the surfactants, which has not been tested.

Other studies of encapsulation by coacervates of pectin and plant protein include an emulsification step. According to Timilsena et al. (2019), a hydrophobic core material is mixed with one of the shell components (mostly the amphiphilic plant protein), and the mixture is homogenised for emulsification. The second shell component (mostly the hydrophilic pectin) is added under conditions limiting the interactions with the protein. Changing pH, temperature or ionic strength of the mixture induces formation of coacervates of pectin and plant protein. Mendanha et al. (2009) encapsulated bitter-tasting casein hydrolysate in such a process in order to reduce the bitterness. They prepared a water - in oil - in water emulsion of casein hydrolysate - in oil - in soy protein solution. Afterwards, dissolved pectin was added and the pH of the mixture was decreased in order to achieve a coacervate formation between pectin and soy protein. Another work from this group (Nori et al., 2011) combined soy protein and pectin for encapsulation of ethanolic propolis extract in a similar way. The question is, however, whether the capsules in these two works were really built from protein-pectin coacervates, or if it was a bilayer formation with an inner emulsifying protein covered by an outer stabilising pectin shell. Such a layer-by-layer process was described by Moser et al. (2020) who tested the encapsulation of buriti oil. They prepared a primary emulsion with chickpea protein and added HMP before a secondary emulsification step and spray-drying. The work found a better physical integrity of the emulsion oil droplets during spray-drying and a higher encapsulation efficiency of the complexes in comparison to pure protein. Ma et al. (2019) prepared real coacervates from citrus pectin and soy protein isolate with and without support by sonication and used them as emulsifiers. The ultrasound-treated coacervates were able to form smaller droplets with a more homogenous size distribution than those prepared without sonication.

Yi et al. (2020) prepared non-covalent binary pea protein – pectin complexes by mixing and heating, loaded them with curcumin (ternary complexes), dispersed the binary or ternary

complexes in the water phase and used them as emulsifier for a ß-carotene containing oil phase. The binary as well as the ternary complexes, resulting from hydrophobic interactions and hydrogen bonding, showed higher emulsion stability and better physical and chemical stability of the ß-carotene than the pea protein alone.

A different method for coacervate preparation was presented by Lan et al. (2020b). Dissolved pea protein isolate and sugar-beet pectin were mixed and used as combined emulsifier for hemp seed oil. The emulsion was prepared by homogenisation, afterwards the pH was adjusted to 2.5 and 3.5, respectively, and the emulsion was kept for equilibration at 4 °C for 24 h. Finally, the sedimented coacervate emulsion was separated and spray-dried. It was found that the physico-chemical properties of the microcapsules were determined by the pH of coacervate formation as well as by the wall / core ratio of the components. Capsules prepared at pH 3.5 had a lower encapsulation efficiency but denser structure and higher mechanical stability than those prepared at pH 2.5 due to stronger electrostatic interactions of pea protein and sugar-beet pectin at the higher pH.

3.2 Nanoparticles

Pectin - plant protein complexes are well suitable for the encapsulation of sensible ingredients. In case the active component is hydrophobic, encapsulation in an amphiphilic matrix allows its stable distribution in a hydrophilic environment. Hydrophobic active ingredients were encapsulated successfully within nanoparticles of the hydrophobic corn protein zein, and these particles were stabilised in a hydrophilic environment by covering them with a hydrophilic pectin shell. Such systems, containing zein and pectin, have been intensively investigated within the last decade and different procedures have been applied for the capsule preparation.

Dhanya et al. (2012) used a combination of zein and a pectic polysaccharide extract from *Coccinia indica* (instead of commercial pectin) for the encapsulation of quercetin. They added the polysaccharide solution drop-wise into an ethanolic zein-quercetin emulsion under sonication and freeze-dried the mixture. Later on (Dhanya et al., 2020) they suspended the resulting amorphous particles in a hydrophilic solution, examined the release of the active ingredient and found a positive effect of the pectin.

A widely applied procedure for preparation of pectin-covered zein-nanoparticles was named as “antisolvent precipitation”. It was used for plant protein and pectin for the first time by Hu et al. (2015). Zein and the hydrophobic active ingredient were dissolved in ethanol and added drop-wise to acidified water, where cationic zein particles were formed. Afterwards, these particles were separated from the suspension and coated with anionic pectin molecules by mixing them with a pectin solution. This method was also applied by other members of the

same group (Xulin Huang et al., 2017; Xulin Huang et al., 2019). The prepared nanocapsules were stable against aggregation and during thermal processing. A combination of 70% pectin and 30% alginate in the polysaccharide coating increased the aggregation stability at pH 5 - 7 and high ionic strength (Xiaoxia Huang et al., 2016). Feng et al. (2020) combined a slightly modified antisolvent precipitation in a system of pectin and zein with ultrasonic treatment for encapsulation of phytosterol. They described the shell of the formed particles as an elastic pectin gel network and the system as stabilised by hydrogen bonds between pectin and zein. Antisolvent precipitation was applied also for the preparation of nanoparticles using the wheat protein gliadin instead of zein in an ethanolic solution (Joye et al., 2015). The nanoparticles were covered with pectin of different DM (61% and 29%) at pH 4.5, and the coating changed their net charge from positive to negative and stabilised them against environmental stress by pH, ionic strength and thermal treatment. LMP coated particles were stronger negatively charged than those with HMP due to the higher negative net charge of the LMP.

Another possible way for covering zein nanoparticles using pectin is the so-called “solvent evaporation method”, as applied by Soltani & Madadlou (2015a; 2015b). Zein and fish oil were dissolved in 80% ethanol and stirred until the ethanol was evaporated, the zein in the remaining nanoparticles enveloped the fish oil. Afterwards, the particles were entrapped in a sugar beet pectin gel matrix by mixing them with a pectin solution and inducing pectin gelation by oxidative crosslinking using laccase. They named the resulting stable product as an “emugel”. It was assumed that there were electrostatic interactions formed between the zein and the pectin.

Chang et al. (2017b) prepared nanoparticles as a ternary complex from two hydrophilic components, pectin and caseinate, and the hydrophobic zein. Solutions containing the three components were mixed under stirring at a defined pH, followed by combined heating and pH-treatment. The nanoparticles were stabilised by hydrophobic and electrostatic interactions and by hydrogen bonds between the three components. The group also tested the effect of encapsulation of curcumin into such complexes, as well as the impact of a chemical protein-pectin crosslinker (Chang et al., 2017a) on the stabilisation of the nanoparticles. The same method for the preparation of ternary complex nanoparticles from pectin, caseinate and zein was used by Veneranda et al. (2018) for the encapsulation of eugenol. They found that hydrophobic and electrostatic interactions were stabilising the nanoparticles during and after nano-spray drying.

A special method of combining pectin and zein in particles was the preparation of gelled microspheres (Liu et al., 2006). An aqueous pectin solution was dripped under stirring into a 75% ethanolic solution containing zein and calcium ions. Pectin beads were formed by the combined action of precipitation by ethanol and formation of calcium bridges, and dissolved zein was incorporated into the particles which were air-dried. The produced beads were loaded

with different ingredients for controlled drug release in the intestine, and it was found, that the zein inhibited swelling of the pectin particles and the pectin protected the zein from digestion by protease. Mukhidinov et al., (2011) applied a similar method and tested the impact of pectin type (citrus, apple) and DM (HMP, LMP) as well as that of zein concentration and type of the bivalent cation (Ca, Zn) on the complex hydrogel beads. They claimed a dominating ionic gelation mechanism for LMP and hydrophobic interactions of HMP, with zein incorporated into the pectin beads. The authors give, however, no clear information about the structure of the pectin capsules and the mechanisms of the interaction of the different pectins with DM from 9 – 52% with the zein. Moreover, the impact of the pectin botanical origin is not clearly discussed.

Some works used pectin - plant protein nanoparticles for preparing pickering emulsions. The theory of these emulsions has been intensively discussed for instance by Dickinson (2010). According to this reference, more or less densely packed and separated or aggregated particles are accumulated at the oil droplet interface and form a protecting and stabilising mono- or multilayer. The author assumed that associative protein-polysaccharide interactions might be highly promising for the preparation of “nanoscale structures” and “core-shell bionanoparticles” for pickering emulsions, and named pectin as one possible polysaccharide source.

Zhou et al. (2018) prepared pectin-zein nanoparticles by antisolvent precipitation and used them for the stabilisation of pickering emulsions. So did Jiang et al. (2019), who found electrostatic interactions between the negatively charged pectin and the positively charged zein and a well-ordered interfacial structure in the emulsion. The authors used two HMP from apple, differing in polydispersity, and found a better stabilisation of the oil phase for the pectin with lower polydispersity and an impact of this parameter on the stabilisation of the oil phase. Zhang et al. (2021) prepared nanoparticles of pectin and zein by a modified antisolvent precipitation method and applied them for the stabilisation of pickering emulsions and protection of lycopene. They varied the DM of the pectin from 13 to 71%, added different amounts of calcium, and found that the DM of the pectin determined the characteristics of the nanoparticles as well as their stabilising properties. Nanoparticles with pectin of DM above 35% formed gel-like pickering emulsions with high long-term stability and good lycopene protection.

A special type of emulsion was prepared from two aqueous phases (water-in-water emulsion of corn starch and guar gum) by Chen et al. (2018) in order to delay starch digestion. The two phases were stabilised by zein-pectin nanoparticles at the interfaces, similar to a pickering emulsion of oil droplets.

3.3 Conjugates

In contrast to all the other presented interactions of plant protein and pectin, the macromolecules in conjugates are covalently bound. Conjugates are applied in order to improve techno-functional properties of proteins and, in particular the stabilisation of interfaces (de Oliveira et al., 2016). There is, however, up to now only a small number of publications covering the formation of conjugates between pectin and plant protein.

Ma et al. (2020) prepared conjugates from citrus or apple pectin with soy protein by dry heating. The pectins were similar in DM but differed in molecular weight, polydispersity and structure of the neutral sugar side chains. The degree of graft, measuring the conjugate formation intensity, was lower for the apple than for the citrus pectin. Probably, the more complex structure of the former pectin was a steric hindrance for the conjugate formation. Nevertheless, the improvement of solubility and emulsifying ability of the soy protein was similar after conjugation with the two pectins, and both conjugates were well suitable for the application as emulsifiers. The authors also tested the formation of a conjugate by heating the same components in solution (wet-heating) and under additional sonication and found an acceleration and higher grafting extent in comparison to tests without ultrasound. Once more, the citrus pectin was superior with respect to the Maillard reaction, but both pectins had a similar effect on the emulsifying ability of the conjugates. Moreover, the authors assumed that the ultrasound treatment supported the conjugation reaction by unfolding the protein (Ma et al., 2020).

Tamnak et al. (2016) tested in two works the properties of pectin - pea protein conjugates formed by dry-heating. They found a lower solubility but higher emulsifying activity of the conjugates in oil-in-water (OW) emulsions, compared to the single components (Tamnak, Mirhosseini, Tan, Ghazali, et al., 2016) as well as in water-in-oil-in-water (WOW) emulsion, where the conjugate was able to replace Tween 80 (Tamnak, Mirhosseini, Tan, Amid, et al., 2016).

Wang et al. (2019) studied conjugates containing citrus pectin and deamidated wheat gluten as protein component. The formed conjugates were able to stabilise emulsions but were less effective than wheat protein – maltodextrin conjugates from the same study.

Li et al. (2021) prepared covalently bound conjugates of potato protein and sugar beet pectin not by dry-heating but by crosslinking using laccase. They improved the foaming ability of the potato protein by reducing the surface tension. It has to be considered, however, that also the applied sugar beet pectin alone should have a certain surface activity.

3.4 Other studied pectin - plant protein systems

Coacervates, nanoparticles and conjugates of plant protein and pectin have been successfully utilised for the stabilisation of emulsions or for the encapsulation of ingredients. Interfacial effects in emulsions and foams have been achieved, however, also by simpler procedures. An amphiphilic protein may be used as surfactant for the emulsion or foam, and the pectin forms a secondary layer around the protein-covered oil droplets or gas bubbles (layer-by-layer-process) due to complex formation with the protein (Gharsallaoui et al., 2010). Bound pectin delays the destabilisation by steric stabilisation and unbound pectin by increasing the viscosity of the aqueous phase around oil droplets or gas bubbles.

An early work on emulsion stabilisation by plant protein – pectin interactions was published by Muschiolik (1989). Faba bean protein was the emulsifier, and the emulsion was mixed afterwards with a pectin solution by ultrasound. The rheology of the emulsion changed, it become more Newtonian, and this property was kept also after heating and freezing. An interaction via calcium ions was assumed as stabilising force. A similar method was applied by Gharsallaoui et al. (2010) in emulsions with pea protein and HMP. They tested not only the formation of complexes in aqueous solution (see section 3.1) but also at an emulsion interface. At low pH and low pectin contents they found destabilisation by bridging flocculation, but at high pectin content the emulsion droplets were stabilised by a secondary coating with a pectin layer. The effect is similar to a bilayer emulsion. Also Zang et al. (2019) reported a stabilising effect of a pectin layer around emulsion droplets prepared with rice bran hydrolysate. They found that the emulsions were stable at different pH and ionic strength and assumed electrostatic and steric repulsion between the droplets. Qiu et al. (2015) tested pectin and xanthan for stabilisation of oil droplets in a bilayer emulsion with wheat gliadin, they found stabilisation at acidic pH, which was reduced at high ionic strength due to lower electrostatic interaction. Comparable results were shown by Xu et al. (2017) who combined rice glutelin as emulsifier with different anionic polysaccharides and found a stabilising effect of pectin also only at low ionic strength.

Other works focused on films and foams containing plant protein and pectin at the interface. A basic investigation on film formation combined soy protein and pectin at the interface (Piazza et al., 2009). It was assumed that an electrostatic protein-pectin interaction at pH 8 - 9 and an increase of the bulk viscosity by pectin improved the interfacial stability. Schmidt et al. (2010) tested foaming of a combination of HMP or LMP with napin from rapeseed at pH 7. At this pH, napin is positively and the pectins are strongly negatively charged with a higher net charge for the LMP. They found that unbound protein at the interface increased the foaming capacity, and the complexes in the bulk mixture increased the foam stability. There was, however, no effect of the DM and, thus, the net charge of the pectin. In another work (Jarpa-Parra et al., 2016), lentil protein and different polysaccharides (including pectin) were

mixed at different pH and the mixtures were used as surfactants in foam formation. At pH 3, a cross-linked gel-like interfacial network was formed. At pH 5, polysaccharide-protein aggregates adsorbed at the interface (comparable to particles at the oil droplets of pickering emulsions), and in both cases foam stability increased. At pH 7, however, stability decreased due to thermodynamic incompatibility of the two macromolecule components.

Finally, some works shall be presented that differed strongly from the other publications. Dekkers et al. (2016, 2018) aimed to the production of fibrous compounds from pectin and soy protein isolate for a possible application as meat-replacer. These works are special due to the high concentration of the components. A blend of soy protein and pectin with a dry matter of 45% was prepared, and a fibrous texture was achieved by shear induced structure formation at temperature > 110 - 140 °C and subsequent cooling (Dekkers et al., 2016; Dekkers et al., 2018). The analysis of the compounds was focused on the structural and viscoelastic properties of the mixture, using microscopy and rheological measurements. Dispersed pectin stabilised the blend, despite it was degraded by ß-elimination. A certain Maillard reaction between the protein and the pectin was indicated by an increase of colour with the reaction temperature. Whether the reaction products might be comparable to conjugates, was not investigated.

A completely different work was published by Zhou et al. (2020). Instead of commercial pectin, they used a LMP-like extract from Premna microphylla turcz with DM 14% and GalA content of 73%, which is popular in southern China. After mixing the separately dissolved pectin and soy protein isolate at room temperature for 2h and storing the mixture overnight, a composite gel was formed. They explained the gelation process by hydrogen bonds and hydrophobic interactions. A low concentration of added sodium favoured the gel formation by a salting-in effect, but a high ion content inhibited the process by electrostatic shielding.

4. Summary and outlook

One aim of the present review was it to give a general overview of the current knowledge in the field of pectin – plant protein interactions. More than 50 publications were included, and most of them have been published within the last decade.

The limited techno-functional properties of plant proteins have been considerably improved by interactions with pectins in various systems. The restricted solubility in aqueous systems around the isoelectric point, in particular of soy and pea proteins, was increased by forming coacervates. Coacervates were also applied to encapsulate active (often hydrophobic) ingredients and to stabilise interfaces of emulsions and foams. It was, however, not always completely clear whether these stabilising complexes were real coacervates or if it were bilayers of plant proteins and pectins. Encapsulation was also achieved by nanoparticles, formed from plant proteins and pectins by various methods. Their hydrophilic pectin core allowed a good long-term stabilisation in an aqueous environment. These nanoparticles were also successfully tested as emulsifiers and stabilisers at interfaces in pickering emulsions. Another group of surface-active pectin – plant protein complexes was prepared by covalent conjugation. All the other pectin – plant protein interactions, electrostatic, hydrogen bonds, hydrophobic interactions and steric effects, were non-covalent. In general, the pectin – plant protein systems were comparable to those of pectins with proteins of animal origin.

Despite of many interesting results, there are open questions and additional subjects that require extended or more detailed investigation. With respect to plant protein sources, important proteins, such as from oat, pumpkin or sunflower, have still not been tested for their interactions with pectin, though commercial products from these sources are available. Some legume proteins, such as from chickpea, lentils or faba bean, have been tested rather seldom, though first results for these materials were encouraging. The application of pectin for reducing the bitterness of the plant protein component, probably by neutralising the negative charge of the protein and, thus, preventing the binding to receptors for bitter taste should be definitely further studied. Bitter taste is a real problem for their incorporation of some plant proteins into food products. Furthermore, the research of the combination of pectin and napin from rapeseed might be intensified, since the untypical high pI of napin allows strong electrostatic interactions with pectin over a broad pH-range from 3 to 10.

The second aim of the review was to focus on a possible impact of pectin type and structure on the interactions with plant proteins. Only 12 out of the more than 50 reviewed works included such investigations. The authors used pectin with differences in botanical source, DM, DB, molecular weight and polydispersity. Some works found an effect of the DM, based on a higher net charge of LMP in comparison to HMP. Other groups reported an inhibiting effect of high polydispersity or molecular weight on the conjugate formation or on the stabilisation ability at the oil-water interface. However, not all of these results were completely plausible. Some of

the tested pectins were commercial samples from different suppliers, which were used without any purification or partly even proper characterisation. There were methodical deficits, or the effects of net charge (DM) and charge density (DB) of the pectins were mixed up. It would be recommended for future tests, to prepare sets of different pectins under controlled and well-documented conditions and to characterise them carefully. This would exclude or at least reduce an undetected additional impact of pectin molecular weight, neutral sugar side chains or of ions added in the modification process and strongly bound to the pectin molecule. These parameters may considerably affect pectin – plant protein interactions.

Moreover, some pectins with special native or modified structure properties have still not been investigated at all for their interactions with plant proteins. No work was found that applied amidated, acetylated, debranched or depolymerised pectin. These modifications alter the charge of the pectin molecule or the molecular flexibility and might strongly affect the interactions with plant protein. Amidated pectins would be able to form more hydrogen bonds due to their amide groups, and acetylated pectins might contribute to more hydrophobic interactions with plant proteins. Debranched pectins with a reduced content of neutral sugars in side chains might show different conjugate formation, and depolymerised pectins with a lower molecular weight might favour conjugate formation but reduce interfacial stabilisation. Even if such systems were of limited commercial interest, their investigation would contribute to a better understanding of the complex interactions of pectin and plant protein.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Ulrike Einhorn-Stoll: Conceptualization, Investigation, Validation, Writing - original draft, Writing - Review & Editing, Supervision. Marina Eichhorn: Investigation, Writing - original draft. Artwin Archut: Investigation, Writing - original draft. Hanna Kastner: Visualization, Writing - Review & Editing, Supervision.

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