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Novel Colloidal Food Ingredients: Protein Complexes and Conjugates

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proteins, polysaccharides, polyphenols, complexes, conjugates, colloidal ingredients

Abstract

Food proteins, polysaccharides, and polyphenols are natural ingredients with different functional attributes. For instance, many proteins are good emulsifiers and gelling agents, many polysaccharides are good thickening and stabilizing agents, and many polyphenols are good antioxidants and antimicrobials. These three kinds of ingredients can be combined into protein, polysaccharide, and/or polyphenol conjugates or complexes using covalent or noncovalent interactions to create novel multifunctional colloidal ingredients with new or improved properties. In this review, the formation, functionality, and potential applications of protein conjugates and complexes are discussed. In particular, the utilization of these colloidal ingredients to stabilize emulsions, control lipid digestion, encapsulate bioactive ingredients, modify textures, and form films is highlighted. Finally, future research needs in this area are briefly proposed. The rational design of protein complexes and conjugates may lead to the development of new functional ingredients that can be used to create more nutritious, sustainable, and healthy foods.

1. INTRODUCTION

Proteins, polysaccharides, and polyphenols are three important functional ingredients found in many foods, which differ in their chemical structures, physical properties, and functional attributes. Many proteins have good emulsifying, gelling, foaming, structuring, and other functional properties. Many polysaccharides have good thickening, gelling, water-holding, and stabilizing properties. Many polyphenols exhibit antioxidant, antimicrobial, and nutraceutical properties. In complex food systems, these three types of ingredients interact with each other, which alters their functionalities. Moreover, new ingredients can be created by rationally assembling colloidal structures from proteins, polysaccharides, and polyphenols. A good understanding of the interactions of these ingredients is therefore useful for the rational design of foods and ingredients with novel or improved functional performances (**Figure 1**). For example, combining proteins and polysaccharides has been shown to improve the solubility, emulsification properties, and thermal stability of the proteins (Chen et al. 2019, Ma et al. 2022) as well as to create delivery systems to encapsulate and protect bioactive components (Li et al. 2022). Similarly, combining proteins and polyphenols has been shown to improve the antioxidant activity of the proteins (X. Sun et al. 2022).

Proteins, polysaccharides, and polyphenols form complexes or conjugates through physical or covalent interactions, respectively (Liu et al. 2017a). Physical bonds are usually reversible, whereas covalent bonds are irreversible. The main advantage of using covalent bonding is that the ingredients formed tend to be more stable to changes in environmental conditions; however, the new

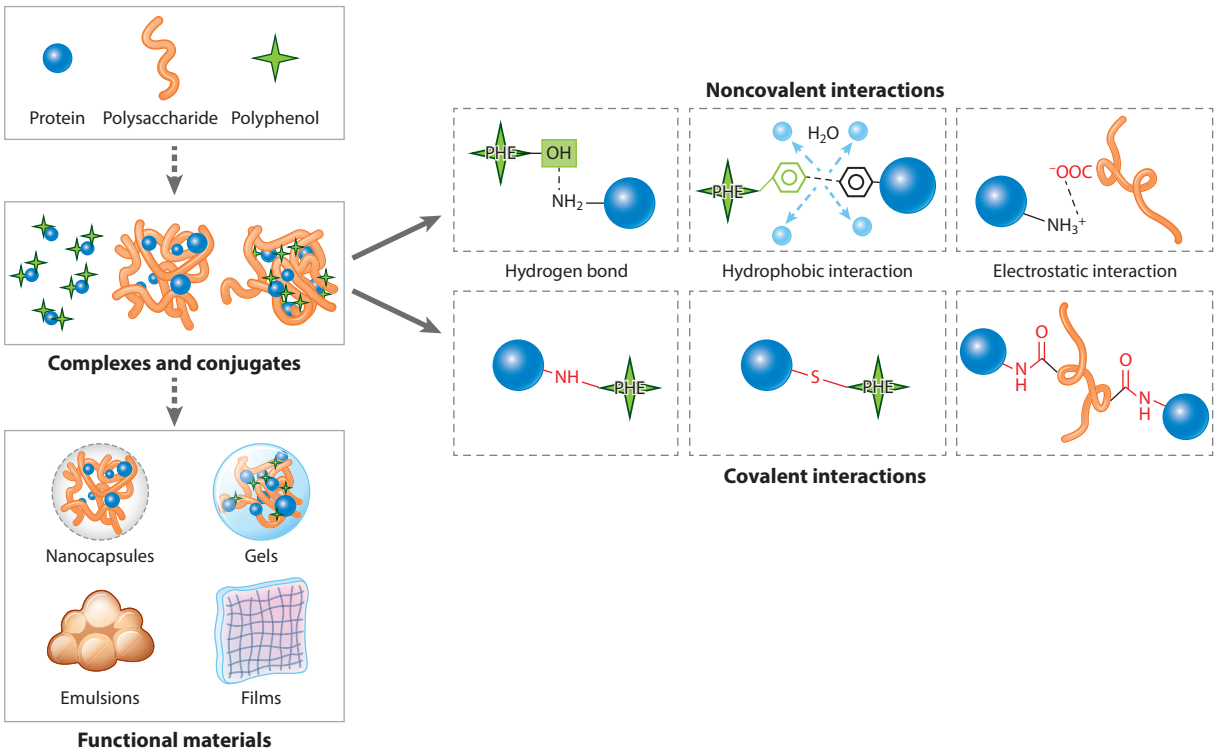

Figure 1

Different kinds of colloidal ingredients can be formed by complexing or conjugating proteins, polyphenols, and/or polysaccharides, which can be used to create novel products such as nanocapsules, gels, emulsions, and films. Abbreviation: PHE, polyphenol.

ingredients formed must meet appropriate regulatory standards. Both chemical methods, such as the Maillard reaction between proteins and polysaccharides (Ma et al. 2021, Y.X. Yang et al. 2015), and enzymatic reactions between proteins and polyphenols (such as laccase or tyrosinase) (X. Li et al. 2020, H. Wang et al. 2022) can be used to promote the formation of covalent bonds between food molecules. The conjugates formed using these processes often combine the beneficial attributes of the individual constituents, such as the surface activity of proteins, the steric stabilization of polysaccharides, and the antioxidant activity of polyphenols (Liu et al. 2016).

Food-grade complexes and conjugates have a variety of potential applications in foods and beverages because of their enhanced functional attributes, such as improved water solubility, thermal stability, surface activity, film-forming, gelling, and preservative properties. In particular, studies have shown that protein–polysaccharide, protein–polyphenol, and protein–polysaccharide–polyphenol complexes and conjugates can be used as multifunctional ingredients such as antioxidant emulsifiers that can form emulsions as well as stabilize them against aggregation and oxidation (Kan et al. 2021, Yan et al. 2020, Zhao et al. 2021). Moreover, they can be used to fabricate colloidal systems designed to encapsulate, protect, and deliver bioactive ingredients in a bioavailable form, such as vitamins, nutraceuticals, and probiotics (Falsafi et al. 2022, S. Ge et al. 2022a, Liu et al. 2017c, W.J. Yan et al. 2021) (**Figure 1**).

In this article, we first review the various ingredients and fabrication methods that can be used to prepare complexes (via noncovalent bonds) and conjugates (via covalent bonds) from proteins, polysaccharides, and/or polyphenols. We then discuss the functional attributes of these colloidal ingredients, including their solubility, stability, emulsifying, foaming, gelling, film formation, antioxidant, and antimicrobial properties. Finally, we discuss the potential applications of these colloidal ingredients in food systems as well as areas where further research is still needed.

2. INGREDIENTS

2.1. Proteins

Proteins are natural polymers consisting of chains of amino acids linked together by peptide bonds. They may come from a variety of sources, including animal products (e.g., meat, fish, egg, and milk proteins), vegetable products (e.g., soy, pea, peanut, sesame, rice, and oat proteins), and microorganisms (e.g., algae protein) (**Figure 2**). The number, type, and sequence of amino acids in the polypeptide chain determine the molecular characteristics of proteins, such as their molecular weight, conformation, flexibility, charge, and hydrophobicity, which in turn govern their functional attributes and biological effects (Liu et al. 2017a). Food proteins are widely used in the food industry for their nutritional value and diverse functional attributes. However, many native proteins have poor solubility, stability, and emulsifying properties and are highly sensitive to changes in the environmental conditions they may experience within foods and the human body, including pH, ionic strength, enzyme activity, and temperature.

2.2. Polysaccharides

Polysaccharides are also natural polymers, but they consist of chains of monosaccharides held together by glycosidic bonds. Like proteins, polysaccharides play an important role in human nutrition and display a diverse range of beneficial functional attributes. They are widely found in plants (e.g., starch, maltodextrin, pectin, and gum arabic), animals (e.g., chondroitin sulfate, hyaluronic acid, and heparin), and microorganisms (e.g., β-glucan, xanthan gum, and mannan) (**Figure 2**). The molecular characteristics of polysaccharides depend on the number, type, sequence, and bonding of the monosaccharides in the chain, which determine their functional attributes (Dedhia et al. 2022). Polysaccharides from different sources also exhibit a broad

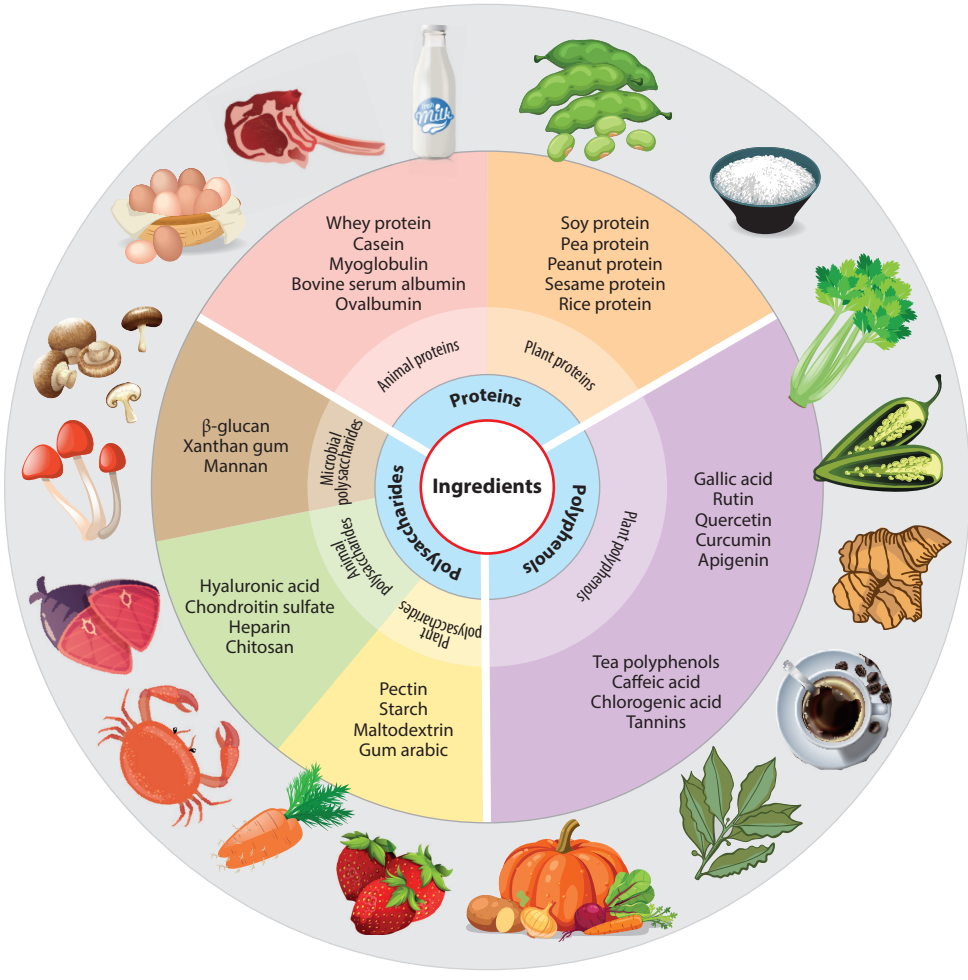

Figure 2

Proteins, polysaccharides, and polyphenols isolated from different food materials.

spectrum of biological activities, including antioxidant, antimicrobial, anticoagulation, anticancer, antivirus, anti-inflammatory, antiradiation, and antitumor activities, which makes them attractive health-promoting components in foods (Yu et al. 2018).

2.3. Polyphenols

Polyphenols are secondary metabolites that are present in many plant-based foods, including fruits, vegetables, grains, legumes, herbs, and spices (**Figure 2**). Polyphenols exhibit a wide range of chemical structures. In general, however, they all have an aromatic ring or a benzene ring with one or more hydroxyl groups attached and can be classified as nonflavonoids (phenolic acids, cinnamic acids, stilbenes, and lignans) or flavonoids. Polyphenols have been reported to exhibit a variety of biological activities that can positively impact human health. For example, their antioxidant and anti-inflammatory activities may help prevent the development of chronic illnesses such as cardiovascular disease, neurodegenerative disease, diabetes, inflammation, osteoporosis, and cancer

(Condezo-Hoyos et al. 2021, Zhang et al. 2020). However, there are several factors currently limiting their widespread utilization as health-promoting ingredients in foods, including their poor solubility, stability, and bioavailability characteristics (Fang & Bhandari 2010, Rambaran 2022).

3. FORMATION OF PROTEIN COMPLEXES AND CONJUGATES

Proteins can be combined with polysaccharides and/or polyphenols through various kinds of physical or covalent interactions, which are discussed in this section.

3.1. Physical Complexation

Noncovalent interactions between proteins and other ingredients typically involve electrostatic interactions, hydrogen bonds, van der Waals forces, π bonds, and hydrophobic interactions (**Figure 3**). Compared to covalent interactions, these physical interactions are often relatively weak and reversible.

3.1.1. Protein–polyphenol complexes. Hydrogen bonding, hydrophobic interactions, and van der Waals forces play a dominant role in the formation of protein–polyphenol complexes. The phenolic groups in polyphenols are good hydrogen donors that can form hydrogen bonds with the C=O groups in proteins (Buitimea-Cantua et al. 2018). Hydrogen bonds can also be formed through interactions between the hydroxyl (−OH) groups of phenolic compounds and the

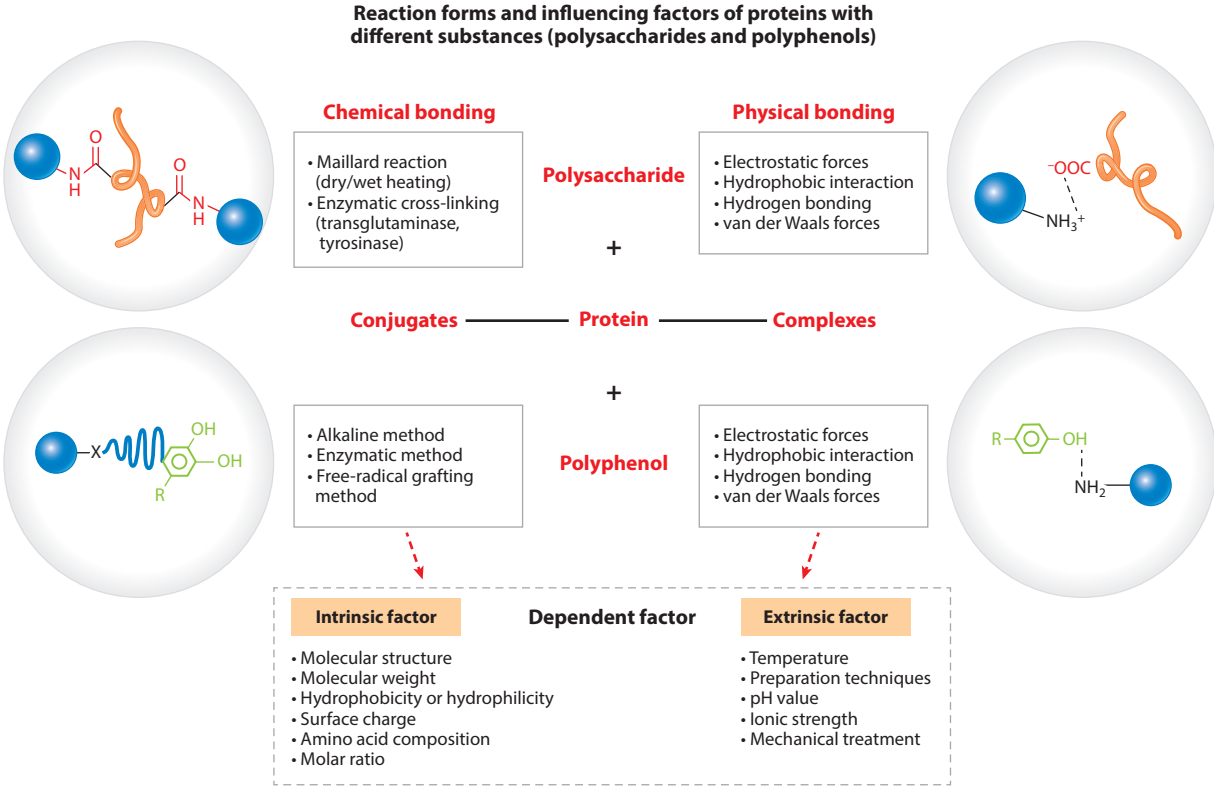

Figure 3

Interactions between proteins, polysaccharides, and polyphenols and the factors influencing them.

hydroxyl (−OH) or amino ($-NH_2$) groups on proteins (Quan et al. 2019). Hydrophobic interactions mainly occur between the nonpolar aromatic rings in polyphenols and the hydrophobic side groups (e.g., leucine, isoleucine, valine, phenylalanine, and tryptophan) in proteins (Baba et al. 2021). van der Waals attractive forces act between all kinds of molecules and may contribute to the overall binding of proteins and polyphenols (Y. Li et al. 2021). For charged polyphenols, electrostatic interactions also play an important role in protein–polyphenol interactions. For instance, negatively charged groups on polyphenols may bind to positively charged groups on proteins. In general, the formation of protein–polyphenol complexes is due to the combined effects of all these different noncovalent associations (Zhang et al. 2021).

3.1.2. Protein–polysaccharide complexes. The formation of protein–polysaccharide complexes is commonly driven by electrostatic attraction between oppositely charged groups on the surface of protein and polysaccharide molecules under appropriate solution conditions, i.e., pH and ionic strength (Jones & McClements 2011). However, van der Waals forces, hydrogen bonding, and hydrophobic attraction also play an important role in the formation and stabilization of some protein–polysaccharide complexes. Proteins and polysaccharides may form soluble complexes, coacervates, or precipitates when they interact with each other through physical forces, depending on their molecular characteristics, molar ratios, and solution conditions (Gentile 2020, Wijaya et al. 2017). Soluble complexes are relatively small entities consisting of only a few proteins and polysaccharides, which are reasonably small in size and possess a large magnitude of surface charge (Wagoner et al. 2016). Coacervates are separate phases consisting of loosely packed proteins and polysaccharides, which can be converted into stable colloidal entities by simple stirring. Precipitates are separate phases consisting of densely packed proteins and polysaccharides, which tend to rapidly sediment.

3.1.3. Protein–polyphenol–polysaccharide complexes. Recently, there has been interest in forming ternary complexes from proteins, polysaccharides, and polyphenols, which can be used as colloidal ingredients in foods (Li & Wang 2015, Liu et al. 2019, W. Yang et al. 2015). Ternary complexes are typically formed by changing the solvent quality, pH, ionic strength, and/or temperature of mixed systems (Santos et al. 2022). Some researchers have reported that the presence of polysaccharides can inhibit protein–polyphenol interactions in solution, which may be useful in preventing the undesirable aggregation of proteins and polyphenols in beverages (Brandao et al. 2017, Carvalho et al. 2006). For instance, the presence of gum arabic and β-cyclodextrin was shown to reduce the binding of procyanidin to α-amylase; however, although the presence of pectin did not prevent binding, it did inhibit the aggregation of the α-amylase-procyanidin complexes formed (Soares et al. 2009). These results suggest that different kinds of polysaccharides affect protein–polyphenol interactions differently. Polyphenols have also been reported to change the interactions of proteins with polysaccharides. For instance, the presence of quercetin led to an increase in β-lactoglobulin (β-LG)–gum acacia binding through a combination of electrostatic and hydrophobic interactions (Aberkane et al. 2012). Other researchers have reported that the presence of epigallocatechin gallate (EGCG) altered the molecular conformation of bovine serum albumin (BSA) in BSA–carrageenan complexes (Li & Wang 2015).

3.2. Covalent Conjugation

Several kinds of protein conjugates exist in nature and can be used as ingredients in the food industry. For instance, gum arabic consists of polysaccharide chains with some protein molecules covalently attached (Hosseini et al. 2015), whereas beet pectin consists of polysaccharide chains with some proteins and ferulic acid covalently attached (Dickinson 2018). Both of these natural molecules are therefore amphiphilic and have been used as emulsifiers in the beverage industry.

The conjugation of proteins to other polysaccharides and polyphenols can also be achieved using chemical (e.g., Maillard, free-radical grafting, and alkaline reactions) or enzymatic (e.g., polyphenoloxidase, laccase, and tyrosinase) approaches (Baba et al. 2021, Liu et al. 2017a). In this case, however, the ingredient manufacturer must consider the regulatory status of the new ingredient formed.

3.2.1. Protein–polyphenol conjugates. Phenolic compounds can react covalently with proteins as either phenolic radicals or quinones (Prigent et al. 2007).

3.2.1.1. Free-radical grafting method. Hydrogen peroxide and ascorbic acid have been used as a redox pair to generate hydroxyl radicals, which can attack the hydrogen atoms in the sulfhydryl and amino groups in the side chains of proteins, thereby generating radical species that can react with polyphenols and form protein–polyphenol conjugates (Liu et al. 2015, Zhang et al. 2021). This method is commonly used because it is relatively rapid, cheap, and ecofriendly.

3.2.1.2. Alkaline reaction method. In this method, polyphenols are incubated within an alkaline solution in the presence of air, which causes them to be oxidized to semiquinones, which then rearrange into quinones. These reactive intermediate products can readily interact with nucleophilic amino acid residues (i.e., methionine, lysine, tryptophan, and cysteine) in the protein chains, thereby resulting in the formation of covalent cross-links (C–N or C–S) between the protein and polyphenol molecules (Quan et al. 2019).

3.2.1.3. Enzyme-catalyzed method. In this method, specific enzymes are used to form covalent links between proteins and polyphenols. For instance, an oxidation reaction catalyzed by polyphenol oxidases (e.g., tyrosinases or laccases) is similar to the alkaline reaction method. Tyrosinase can first react with monophenols and polyphenols to form semiquinone or quinone intermediates, which are then attacked by nucleophiles on the proteins to generate covalent bonds between the molecules (X. Li et al. 2020). Quinones can also be formed enzymatically using laccases, which then oxidize substrates with a *p*-bisphenol structure (Prigent et al. 2007).

3.2.2. Protein–polysaccharide conjugates. Food grade protein–polysaccharide conjugates can be produced through chemical methods or enzymatic methods (**Figure 3**).

3.2.2.1. Maillard reaction. Protein–polysaccharide conjugates are prepared using the Maillard reaction under controlled time, temperature, pH, and moisture conditions (de Oliveira et al. 2016). The most common approaches used for preparing Maillard-type conjugates are dry heating of biopolymer mixtures under controlled temperature and relative humidity conditions as well as wet heating of these mixtures in alkaline aqueous solutions (Li et al. 2013). The Maillard reaction involves a complex series of reactions that does not require any additional chemicals (Spotti et al. 2014). Initially, a condensation reaction occurs between available amino groups on the proteins (such as the ε-amino group of lysine residues or the α-amino groups of terminal amino acids) and reducing sugar groups on the polysaccharides to form an *N*-substituted glycosylamine. This compound is in equilibrium with an unstable Schiff base, which further rearranges to form Amadori products (Sedaghat Doost et al. 2019, Xiao et al. 2018). The rearrangement compounds are degraded in various ways depending on the pH of the system, resulting in brown nitrogenous compounds and copolymers (Martins et al. 2000). The reaction conditions (e.g., pH, temperature, relative humidity, and time) should be optimized to prevent the generation of antinutritional and toxic reaction compounds (such as melanins and acrylamide) so as to obtain Maillard-type conjugates with the required functional attributes (Gentile 2020).

3.2.2.2. Enzyme-catalyzed reactions. Protein–polysaccharide conjugates can also be obtained using enzyme-catalyzed reactions. For instance, the aromatic amino acid groups on proteins and the phenolic groups (ferulic acids) on polysaccharides can form covalent bonds in the presence of oxidases such as tyrosinase, laccase, and peroxidase (Chen et al. 2002, Wei & Huang 2019). Transglutaminase can catalyze the formation of covalent bonds between lysine and glutamine groups in proteins (Jung & Wicker 2012) as well as between the amino groups in chitosan and the glutamine in proteins.

3.2.3. Protein–polyphenol–polysaccharide conjugates. Different strategies have been developed to form ternary conjugates consisting of proteins, polysaccharides, and polyphenols. For example, protein–polysaccharide conjugates can first be formed using the Maillard reaction, and then polyphenols can be covalently attached (Liu et al. 2017a). It has been reported that the surface hydrophobicity of myofibrillar protein–dextran conjugates is increased after polyphenols (EGCG, catechin, and gallic acid) are covalently attached, whereas the free amino and thiol groups and tyrosine residues decreased (Y. Xu et al. 2021). Alternatively, protein–polyphenol conjugates can be formed, and then polysaccharides can be covalently attached (Liu et al. 2017a). For example, a combination of an alkaline treatment and the Maillard reaction was used to fabricate chlorogenic acid–lactoferrin–glucose/polydextrose conjugates (Liu et al. 2015, 2016) and BSA–chlorogenic acid–dextran conjugates (Yan et al. 2020), which were shown to be effective antioxidant emulsifiers. In some cases, both covalent and noncovalent interactions can be used to assemble ternary complexes (Y. Zhao et al. 2020).

3.3. Factors Affecting Protein Complex and Conjugate Formation

The effects of the formation of protein complexes and conjugates depend on various factors (**Figure 3**), including the nature and molar ratio of the different components (e.g., proteins, polysaccharides, and/or polyphenols), and environmental conditions (e.g., temperature, pH, and ionic strength, shearing, etc.).

3.3.1. Internal factors. The internal factors are the intrinsic properties and molar ratios of the proteins, polysaccharides, and/or polyphenols used to assemble the conjugates or complexes. For instance, the size, shape, hydrophobicity, flexibility, and charge of proteins impact their binding behavior (Prigent et al. 2003, Ye 2008). As an example, a higher binding affinity of tea polyphenols was reported to β-casein than to α-casein, which was attributed to the more hydrophobic nature of β-casein (Hasni et al. 2011). Hydrolyzing rice protein was reported to lower its tendency to form Maillard conjugates, which may be because the lysine residues moved to a more hydrophobic environment, thereby reducing their ability to react with polysaccharides (Stone et al. 2013). The accessibility of the target residues is also crucial for conjugation reactions. For example, a tyrosine located at the end of a polypeptide chain is more available for cross-linking than one located in the middle, which has been attributed to steric hindrance effects (Jung & Wicker 2012).

The structural features of phenolic acids, including their size, hydroxylation, methoxylation, glycosylation, methylation, flexibility, and steric hindrance, have been reported to affect their interaction with proteins (T. Li et al. 2020, Naczk et al. 2011). Another study showed that the noncovalent interactions of β-LG with flavonoids depended on their precise molecular structures, such as the position of their functional groups on the phenyl rings (Li et al. 2018). Similarly, the binding of phenolic acids to bovine serum proteins has been shown to depend on the precise location of the functional groups on the benzene ring (Yuan et al. 2019). The binding affinity of polyphenols to proteins has been reported to increase as their dimensions increased, which can be attributed to an increase in the attractive forces and a reduction in the entropy of mixing effects

(Hasni et al. 2011, Soares et al. 2007). These molecular differences mean that polyphenols extracted from different botanical sources and/or from different plant parts may interact differently with proteins (Naczk et al. 2011).

The molecular characteristics of polysaccharides also impact their ability to form complexes and conjugates. The efficiency of conjugate formation has been reported to increase as the molecular weight of polysaccharides decreases because there are then more reductive terminal carbonyl sites per unit mass of polysaccharide (de Oliveira et al. 2016, Jiménez-Castaño et al. 2007). The electrical properties of polysaccharides also impact complex formation. For instance, the binding of ovalbumin (OVA) to carboxymethylcellulose (CMC) was reported to increase when the charge density of the CMC increased (Xiong et al. 2017).

The concentrations of proteins, polysaccharides, and polyphenols also affect the nature of the conjugates or complexes formed. For instance, the binding of lactoferrin to oat β-glucan was reported to decrease at high polysaccharide concentrations, which was attributed to the fact that greater chain entanglements reduced the number of protein binding sites available on the β-glucan molecules (Yang et al. 2020). Other researchers have reported that the solubility, emulsifying activity index, and emulsion stability index of soy protein–EGCG conjugates first increased and then decreased as the polyphenol concentration was increased (S.Z. Yan et al. 2021). Taken together, these results highlight the importance of optimizing the type and concentration of components used.

3.3.2. External factors. External factors include the environmental conditions used during the complexation or conjugation reactions, including temperature, pH, ionic strength, etc.

3.3.2.1. Temperature. Temperature affects the interactions between proteins, polysaccharides, and polyphenols by altering their solubilities, conformations, and interaction strengths. In general, lower temperatures favor hydrogen bonding, whereas higher ones favor hydrophobic interactions (Wijaya et al. 2017). For instance, β-LG showed a stronger affinity for EGCG at higher temperatures, which was attributed to an increase in the surface hydrophobicity of the proteins due to partial unfolding as well as to a strengthening of the hydrophobic attraction (Wang et al. 2007). However, if globular proteins are heated at a high temperature, they aggregate, which reduces the number of hydrophobic sites available for interaction with polyphenols. Researchers have reported that the binding affinity of quercetin and chlorogenic acid to BSA diminished after heat denaturation of the globular proteins, which could be a result of this aggregation effect (Rawel et al. 2005). Overall, the effects of temperature on conjugation and complexation depend on the nature of the proteins and ligands used. The potential for thermal treatments to promote the oxidation of phenolic compounds, resulting in the formation of semiquinones and quinines, should also be considered when carrying out these reactions.

Increasing the temperature has been reported to enhance the formation of hydrophobic bonds between proteins and polysaccharides (Li et al. 2017, Wijaya et al. 2017). Temperature is also an important factor in the formation and functionality of Maillard conjugates. Higher temperatures can increase the number of reactive amino groups exposed to carbonyl groups due to partial unfolding of the protein structure, as well as increase the chemical reactivity of the carbonyl groups (Sedaghat Doost et al. 2019). The most important factors that have been reported to impact the degree of glycation in Maillard conjugates are temperature, relative humidity, time, and molar ratio (Martinez-Alvarenga et al. 2014). For instance, heating has been shown to increase the number of protein molecules attached to tea polysaccharides, thereby improving their solubility and emulsifying properties (Q. Li et al. 2021). For enzyme-induced reactions, a thermal treatment of β-LG

was shown to increase the exposure of tyrosine residues and thereby enhance the laccase-catalyzed formation of protein–sugar beet pectin conjugates (Jung & Wicker 2012).

3.3.2.2. pH. The pH affects the charge, structure, and interactions of proteins and their ligands. For instance, studies have shown that the binding of ferulic acid to β-LG in the monomer form at pH 2.4 is much stronger than in the dimer form at pH 7.3 (Abdollahi et al. 2020). Molecular dynamics simulations have suggested that ferulic acid had more sites of interaction on the monomer surfaces than on the dimer surface. Another study reported that hydrophobic attraction was the major force involved in the formation of wheat gliadin and quercetin complexes at pH 2 to 4, whereas hydrogen bonding and van der Waals forces were more dominant at pH 5 to 9 (Q. Wang et al. 2020). In addition, polyphenols are easily oxidized to reactive radicals and quinones under alkaline pH conditions, which can covalently interact with proteins (Ozdal et al. 2013, Wang et al. 2014).

The pH also plays an important role in the formation and properties of polysaccharide–protein complexes, which is mainly due to its influence on the electrostatic interactions between the molecules. The electrical charge on proteins goes from positive below their isoelectric point to negative above it. In contrast, the electrical charge on ionized polysaccharides tends to persist over a wider pH range. For instance, pectin and alginate are negatively charged from below pH 3 to above pH 8. Proteins and anionic polysaccharides therefore interact with each other through electrostatic attraction at pH values around and below the isoelectric point of the protein molecules. Conversely, proteins and cationic polysaccharides tend to interact with each other at pH values around and above the isoelectric point. The nature of the complexes formed also depends on the pH. Soluble complexes, coacervates, or precipitates may form depending on the strength and number of attractive electrostatic interactions involved (Stone et al. 2013, Wei & Huang 2019). For instance, researchers have shown that coacervates form between whey proteins and basil seed gum around pH 5.0 but soluble complexes form around pH 6.0 (Behrouzain et al. 2020). In another study, it was shown that the yield of OVA–CMC complex coacervates formed was around 68% and 55% at pH 3.0 and 3.5, respectively (Xiong et al. 2020). When the pH was increased to 4.0, the CMC became more negatively charged, whereas the OVA had fewer positive charges, which resulted in a low yield of coacervates. The pH may also influence the rate of chemical reactions used in conjugation. For instance, it was reported that the Maillard reactivity increased with pH in ribose–arginine (Geng et al. 2019) and lysine–fructose (Ajandouz et al. 2001) systems.

3.3.2.3. Ionic strength. The ionic strength also influences the interactions between charged molecules in solution by exerting an electrostatic screening effect. Studies have shown that a low ionic strength can promote the formation of intermolecular soluble complexes (Li et al. 2012, Souza & Garcia-Rojas 2017, Xiong et al. 2017), which was attributed to screening of the medium- and long-range repulsive interactions between the biopolymers, thereby promoting their bridging (Li et al. 2012, Seyrek et al. 2003). However, increasing the ionic strength above a critical level screens the short-range attraction between polymers, resulting in the suppression of complex formation (Li et al. 2012, 2017). Researchers reported that a lower salt concentration (NaCl < 50 mM) promoted the formation of OVA and glucan sulfate coacervates, whereas higher salt concentration (50–400 mM) inhibited their formation because of electrostatic shielding effects (Liu et al. 2021).

The ionic strength of a solution also impacts the interactions between proteins and polyphenols. Increasing the ionic strength from 10 to 500 mM was reported to decrease BSA–tannin complexation, suggesting that electrostatic forces played a major role in their formation (de Freitas et al. 2003). The addition of calcium ions has been reported to promote EGCG/β-LG interactions,

leading to the formation of complexes (Carnovale et al. 2015). This effect was mainly attributed to the ability of cationic calcium ions to form bridges between anionic protein and EGCG molecules. At high ionic strengths, BSA molecules tend to unfold, which may expose buried hydrophobic amino acid residues that can interact with phenolic compounds (Rawel et al. 2005).

3.3.3. Processing treatments. Physical processing treatments, such as shearing (Ach et al. 2015), sonication (Yildiz et al. 2018), and microfluidization (G.-Y. Li et al. 2021), can modulate the properties of noncovalent protein complexes. For instance, vortex fluidic devices have been shown to promote the interactions between the molecules in protein–polysaccharide coacervates, resulting in an increased elastic modulus (G.-Y. Li et al. 2021). Several studies have shown that the processing treatments, including sonication (Qu et al. 2018), microwaving (Nasrollahzadeh et al. 2017), high pressures (Avila Ruiz et al. 2016), and pulse electric fields (Jian et al. 2018), can also be used to accelerate grafting reactions and improve conjugate functionality.

4. PROPERTIES OF COMPLEXES AND CONJUGATES

The interactions between proteins, polysaccharides, and/or polyphenols can be controlled to create complexes or conjugates with new or improved functional attributes (**Figure 4**). Currently, the most studied functional attributes of complexes or conjugates are their physical characteristics, functional properties, and biological effects, so we focus on these attributes below.

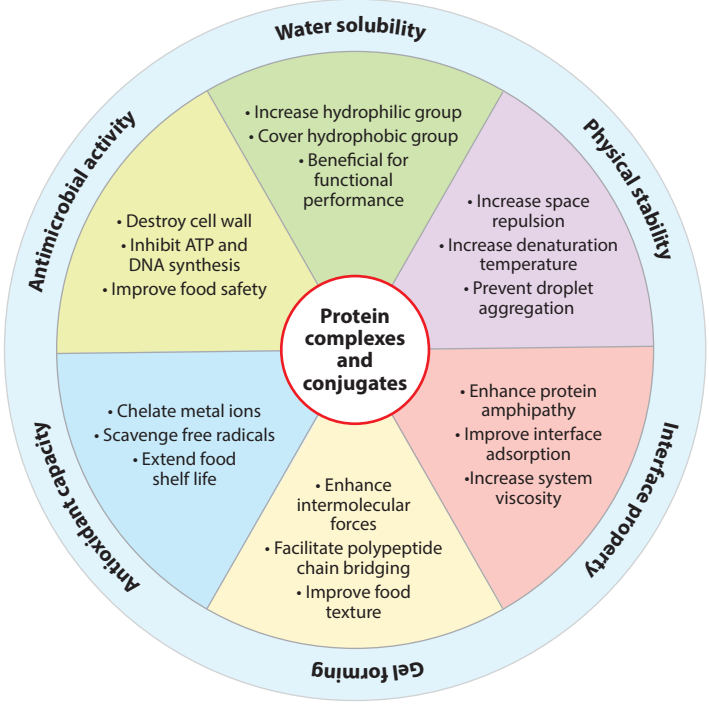

Figure 4

Functional properties of protein complexes and conjugates.

4.1. Physical Properties

The formation of protein complexes or conjugates greatly affects the physical characteristics of proteins, including water solubility, rheological properties, and thermal stability.

4.1.1. Water solubility. The solubility of proteins in water is critical for many of their functional attributes, including emulsification, foaming, gelling, and digestion. The application of many proteins, especially those derived from plants, is often limited because of their poor solubility characteristics (Chao & Aluko 2018). Consequently, it is important to be able to improve the water solubility of these proteins. The solubility of proteins can be improved by combining them with polysaccharides. For instance, researchers have reported that complexes formed from pearl oyster proteins and polysaccharides (pectin, κ-carrageenan, and sodium alginate) had better solubility than the proteins alone (Xue et al. 2020). The solubility of complexes also depends on protein:polysaccharide ratio and pH. For instance, the solubility of pea protein–gum arabic conjugates was higher than that of pure pea protein around the protein's isoelectric point (pH 4.5–7) and under strongly alkaline conditions (pH 11) but not at other pH values (Shen et al. 2022).

Protein–polyphenol interactions can also change the solubility of proteins. For instance, the addition of rutin and quercetin reduced the solubility of myofibrillar protein because these phenols promoted protein cross-linking (J. Cheng et al. 2020). However, some hydrophilic polyphenols can reduce the surface hydrophobicity of proteins and increase their solubility. For instance, the binding of gallotannic acid and EGCG to myofibrillar proteins through hydrogen bonding increased the water solubility of the proteins (Q.D. Xu et al. 2021).

4.1.2. Rheological properties. Interactions of proteins with polysaccharides and/or polyphenols can also alter the rheological properties of proteins, including their viscosity and viscoelastic properties (Warnakulasuriya & Nickerson 2018, Zhang et al. 2019). For instance, a stronger gel network was formed when xanthan gum was mixed with peanut proteins (Jiao et al. 2018). Other researchers reported that the conjugation of purified polyphenols and heat-treated seed kernel proteins reduced the thickening properties of the proteins (Yan et al. 2022). Thus, these effects appear to depend on protein, polysaccharide, and polyphenol type as well as environmental conditions.

4.1.3. Thermal stability. Thermal processing operations are widely applied in the manufacture of protein-rich foods and beverages. Consequently, it is important to understand the impact of heating on the stability, aggregation, and functionality of proteins. The thermal stability of proteins can be improved by forming complexes or conjugates with polysaccharides because of the increased steric repulsion provided by the hydrophilic polysaccharide chains. The electrostatic complexation of soybean proteins with anionic polysaccharides (acacia gum, sodium alginate, and soybean soluble polysaccharides) was shown to improve the thermal stability of the proteins through a similar mechanism (D. Li et al. 2020). Polyphenols can also be used to enhance the thermal stability of proteins. For instance, Pham et al. (2019) reported that conjugation of flaxseed proteins with flaxseed polyphenols, ferulic acid, or hydroxytyrosol improved their thermal stability. Conjugation of EGCG to zein was reported to increase the thermal stability of the proteins, but complexation of EGCG had the opposite effect, which was attributed to changes in the structure of the proteins caused by the noncovalent attachment of the polyphenols (Liu et al. 2017b).

4.2. Functional Properties

Proteins, polysaccharides, and polyphenols possess their own excellent functional properties. The interaction between them may generate new complexes or conjugates with unique or multifunctional properties such as emulsifying, foaming, gelling, and film-forming properties.

4.2.1. Emulsifying properties. Many food proteins are amphiphilic molecules that can adsorb to oil–water interfaces and reduce the interfacial tension. Moreover, they can generate electrostatic and steric repulsion between the droplets. As a result, they can be used to form and stabilize emulsions. However, protein-stabilized emulsions are highly sensitive to environmental stresses such as pH, ionic strength, heating, and freezing–thawing. Protein complexes and conjugates have been shown to have better emulsifying properties than pure proteins. The covalent attachment of polysaccharides to proteins changes the conformation and surface chemistry of the protein, thereby enhancing its ability to form and stabilize emulsions (Oliver et al. 2006, Qu et al. 2018).

In some cases, polyphenols can also improve the emulsification properties of proteins by adsorbing to their surfaces, altering their surface hydrophobicity and interdroplet interactions. For instance, noncovalent binding of egg white proteins to tea polyphenols significantly improved their emulsification properties (J. Sun et al. 2022).

4.2.2. Foaming properties. Many food proteins can adsorb to air–water interfaces, reduce the interfacial tension, and form protective coatings around air bubbles. Consequently, they can be used as foaming agents to form and stabilize food foams, such as whipped cream, beer head, and bread. The addition of polysaccharides can improve the foaming properties of proteins by promoting the diffusion of the proteins from the aqueous phase to the bubble surfaces and by increasing the viscosity and thickness of the adsorbed layer, thereby inhibiting aggregation and Ostwald ripening (W. He et al. 2021, Ho et al. 2021). Electrostatic complexes formed from linseed protein and linseed gum have a higher solubility than the pure proteins, which improved their foaming capacity and foam stability performance (Nikbakht Nasrabadi et al. 2020). Polyphenols can also improve the foaming properties of proteins. For instance, they can bind to protein surfaces, promote partial protein unfolding, and increase interfacial rheology, thereby improving their ability to form and stabilize foams (Cao et al. 2018, C. Li et al. 2021). EGCG, chlorogenic acid, gallic acid, and resveratrol have also been reported to improve the foaming performance of food proteins such as pea and whey proteins (Chen & Ma 2020, Hao et al. 2022).

4.2.3. Gelling properties. Food proteins can be gelled under certain conditions by forming a 3D network of protein molecules held together by covalent and/or noncovalent bonds. The gelling properties of proteins play an important role in determining the texture and mouthfeel of many food products, such as jellies, tofu, cheese, and yogurt. The nature of the gels formed, such as their appearance, texture, and water-holding properties, is often determined by the pH, ionic strength, and temperature used. Polysaccharides can change the gelling properties of proteins by altering their conformations and interactions. The electrostatic and hydrogen-bonding interactions between casein and κ-carrageenan have been reported to lead to the formation of a compact gel network that significantly improves the texture of the final product (Tang et al. 2019). The complexation of galactomannan and soy protein was shown to improve the gelation properties of the proteins, depending on the concentration and molecular weight of the polysaccharide used (Lopes-da-Silva & Monteiro 2019).

Polyphenols can also influence the gelation properties of proteins through covalent and noncovalent interactions. Oxidized gallic acid was reported to enhance the gelation of myofibrillar proteins by promoting disulfide bond formation between polypeptide chains, and EGCG addition was shown to promote the formation of hydrogen-bonding and hydrophobic interactions that enhanced the gelation properties of the myofibrillar protein (Y. Xu et al. 2021).

4.2.4. Film-forming properties. The ability of proteins to aggregate with each other can also be utilized to form thin films. Typically, a protein solution is spread onto a surface and then the solvent is evaporated, which promotes protein aggregation and film formation. However, the films

formed often do not have the structural, physicochemical, or functional properties required for food applications. Complexation or conjugation of proteins can often improve their film-forming and mechanical properties (Shen et al. 2021, Zhang et al. 2019). For instance, the complexation of zein with gum exudates was shown to improve their film-forming properties (da Silva et al. 2020). In another study, it was shown that the addition of oxidized ferulic or tannic acid improved the film-forming properties of whey proteins by promoting covalent cross-linking of the proteins (Wang & Xiong 2021). Consequently, both polysaccharides and polyphenols may be used either individually or in combination to improve the film-forming performance of proteins, which may be useful for the creation of edible coatings or biodegradable packaging materials for food applications.

4.3. Biological Effects

In addition to physical and functional properties, as demonstrated by in vitro and in vivo evidence, proteins also interact with polysaccharides and/or polyphenols to change the biological effects of complexes or conjugates, including bioaccessibility, antioxidant activity, antimicrobial properties, and immunogenicity.

4.3.1. Bioaccessibility. The bioaccessibility of a protein depends on its digestion and absorption within the gastrointestinal tract, which influences its nutritional value. Polysaccharides and polyphenols can influence the bioaccessibility of protein. The formation of physical complexes between whey proteins and *Flammulina velutipes* polysaccharides was shown to inhibit protein digestion under gastric conditions but not under small intestine conditions, which can be utilized to enhance the satiety of beverages (Shang et al. 2020). Similar results were reported for whey protein–*Tremella fuciformis* polysaccharide complexes (Hu et al. 2019). These effects can be attributed to several mechanisms, including the ability of polysaccharides to thicken gastrointestinal fluids, form a physical barrier between proteins and proteases, and bind critical gastrointestinal components (Lin et al. 2019). Polyphenols can also impact the bioavailability of proteins. Chlorogenic acid has been shown to promote conformational changes in whey proteins and caseins, which increased the accessibility of protease binding sites, thereby improving protein digestibility (Jiang et al. 2018). Polyphenols extracted from fruits and vegetables have been shown to reduce the digestion of proteins, which may be due to their ability to bind to and inhibit proteases (Dufour et al. 2018). In the future, it would be useful to systematically investigate the effects of other polyphenols and polysaccharides on protein digestibility and absorption, as this may be a useful means of impacting the satiety response and bioavailability of protein-rich foods.

4.3.2. Antioxidant activity. Antioxidants prevent or delay oxidation reactions, thereby improving food quality, prolonging shelf lives, and increasing food safety. Many proteins exhibit antioxidant activities and can therefore be used as natural antioxidants; however, their potency is often rather limited. For this reason, there has been interest in improving their effectiveness by combining them with polysaccharides or polyphenols. P.P. Wang et al. (2020) fabricated whey protein–mulberry fruit polysaccharide conjugates using the Maillard reaction. The conjugates had a significantly higher antioxidant activity than the pure proteins, which was mainly attributed to conformational changes in the proteins that exposed antioxidant amino acids. The complexation of whey proteins with EGCG and caffeic acid has also been shown to increase their antioxidant activity (de Morais et al. 2020). Moreover, the complexation of soy proteins with polyphenols extracted from a variety of plants has been shown to increase their antioxidant properties (de Souza et al. 2020, Han et al. 2018, Maryam Adilah & Nur Hanani 2019).

4.3.3. Antimicrobial properties. Antimicrobial food ingredients influence the quality, safety, and shelf lives of protein-based foods. Several proteins and peptides naturally exhibit antimicrobial activities, which has been attributed to their ability to increase the cell membrane permeabilities, resulting in an outflow of cytoplasmic components, which interferes with critical metabolic processes and inhibits ATP and DNA synthesis (Motelica et al. 2020). Nevertheless, the antimicrobial properties of many proteins are relatively limited. Combining proteins with polysaccharides and polyphenols is therefore being explored as a means of increasing their antimicrobial properties. T. Lin et al. (2022) reported that complexing lactoferrin with soybean soluble polysaccharides improved the thermal stability and antibacterial activity of lactoferrin so that the complex retained its antibacterial activity after thermal treatment. Jansen-Alves et al. (2019) prepared microparticles using propolis extract and pea protein, which exhibited improved antimicrobial effects against *Staphylococcus aureus* and *Listeria monocytogenes*.

4.3.4. Immunogenicity. Proteins containing high levels of aromatic amino acids (especially tyrosine) have strong immunogenicity effects, thereby resulting in food allergies and restricted use. Typically, food allergies are triggered by the ability of IgE antibodies to recognize antigens, which leads to degranulation of mast cells or basophils and the release of proinflammatory mediators. Protein allergenicity may be reduced by blocking the IgE binding sites for the protein allergens using polysaccharides and/or polyphenols. For instance, the conjugation of dextran to whey protein has been shown to reduce the binding ability of IgE because of steric hindrance effects (Xu et al. 2018).

Phenolic compounds can also change protein immunogenicity by altering or shielding IgE binding sites. For instance, tannins can interact with gluten and reduce the intestinal inflammation associated with celiac disease (Girard & Awika 2020). Pan et al. (2022) confirmed that combining plant polyphenols with food proteins could reduce their allergenicity. In the future, it would be useful to carry out further in vitro and in vivo studies on the impact of polyphenols and polysaccharides on the allergenicity of a variety of food proteins.

5. APPLICATIONS OF PROTEIN COMPLEXES AND CONJUGATES

Protein complexes and conjugates have been finding increasing utilization as functional ingredients in food applications (**Figure 5**). Some of their most promising potential applications are highlighted in this section.

5.1. Emulsion Stabilization

Protein complexes and conjugates can be used to form and stabilize Pickering emulsions and high internal phase emulsions (HIPEs) because of their ability to adsorb to oil–water interfaces and form protective coatings (Livney 2010, Tang 2021). The addition of anionic pectin to acidic milk beverages significantly reduces the aggregation of protein-coated oil droplets and free proteins because the polysaccharide molecules interact with the proteins and increase the electrostatic and steric repulsion between them (Guo et al. 2021). Zein–gum arabic Maillard conjugates have been shown to improve the water dispersibility of the zein as well as to successfully form and stabilize semisolid Pickering HIPEs (Ma et al. 2021). Noncovalent and/or covalent attachment of polyphenols to proteins can lead to the formation of antioxidant emulsifiers that improve both the physical and chemical stability of emulsions (Y. Li et al. 2021). The interfacial properties of some proteins can also be improved by forming protein–polyphenol complexes (Dai et al. 2022). For example, physical mixtures of pea proteins and grape seed proanthocyanidins can form and stabilize Pickering emulsions (Dai et al. 2020). Other researchers reported that crystalline curcumin

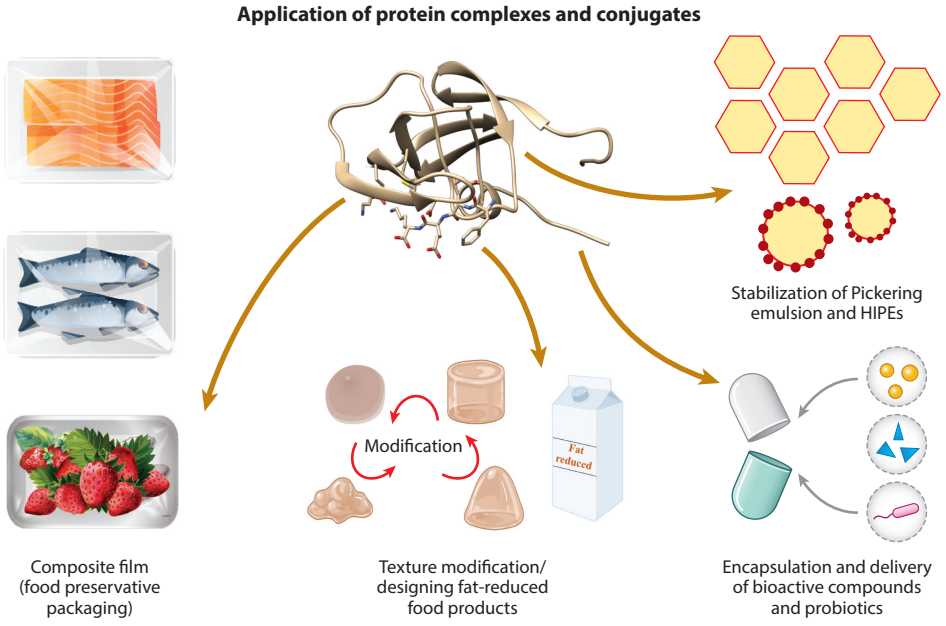

Figure 5

Examples of applications of protein complexes and conjugates in food systems. Abbreviation: HIPEs, high internal phase emulsions.

and quercetin improved the ability of whey proteins to form and stabilize Pickering emulsions (Zembyla et al. 2019). Overall, a variety of protein–polyphenol conjugates have been formed that exhibit excellent emulsifying and antioxidant properties (Quan et al. 2019). Other researchers have shown that these conjugates can also be used to produce HIPEs that are resistant to heating, freezing, and long-term storage and encapsulate, protect, and deliver probiotics (Peng & Tang 2020, Qin et al. 2021a).

Recently, Pickering and/or HIPEs stabilized by protein–polysaccharide–polyphenol ternary complexes have received extensive attention. Peppermint oil emulsions have been formed and stabilized by zein–pectin–resveratrol particles (H. Cheng et al. 2020). The pectin improved the emulsifying properties of the zein, whereas the resveratrol improved its antimicrobial properties. Feng et al. (2021) reported that the aggregation of oil droplets in HIPEs stabilized by pea protein–pectin–EGCG complexes could be effectively inhibited during long-term storage. These reports suggest that protein–polysaccharide–polyphenol complexes are a viable option for forming and stabilizing Pickering emulsions and HIPEs.

5.2. Controlling Digestion of Lipids

The addition of polysaccharides or polyphenols can be used to alter the digestibility of protein-coated lipid droplets, which may be useful for manipulating their gastrointestinal fate. For instance, researchers have shown that the digestibility of lipids in oil-in-water emulsions could be reduced by combining whey protein and dextrin (Hu et al. 2022). Other researchers reported that glycosylation of whey proteins can enhance the digestibility of conjugated linoleic acid by increasing its release rate in the stomach and small intestine (S. Ge et al. 2022a). In this case, the polysaccharides inhibit droplet flocculation, thereby increasing the surface area of lipids

exposed to the digestive enzymes. The extent of this effect depends on the type and concentration of polysaccharides used (Xu et al. 2020). In contrast, alginate–chitosan–β-LG interfacial complexes have been shown to reduce the rate and extent of lipid digestion under simulated gastrointestinal conditions, which was attributed to their ability to inhibit lipase adsorption (Li & McClements 2011). The rate and extent of lipid digestion in emulsions have also been inhibited by coating the oil droplets with colloidal particles assembled from zein–polyphenol conjugates, which was attributed to a similar effect (S. Ge et al. 2022b). These results indicate that lipid digestion can be modulated by controlling the nature of complexes or conjugates at the oil droplet surfaces.

5.3. Encapsulation, Protection, and Delivery of Bioactive Substances

Encapsulation technologies are often needed to protect and deliver bioactive substances like vitamins, nutraceuticals, probiotics, and preservatives (McClements 2015, Poon et al. 2020). Lipophilic bioactive components can be encapsulated within oil-in-water emulsions stabilized by protein-based complexes and conjugates (Fu et al. 2019, S. Li et al. 2021). They can also be encapsulated within emulsion gels formed by gelling the aqueous phase of these emulsions (D. Lin et al. 2022, Liu et al. 2022). Hydrophilic bioactive components can be encapsulated within hydrogel systems assembled from proteins and/or polysaccharides. Recently, many researchers have focused on using protein-based complexes and conjugates to design delivery systems for bioactive substances. For example, strong gels formed by cross-linking sodium alginate and whey protein with transglutaminase and calcium ions were shown to improve the photostability, gastrointestinal stability, and anti-inflammatory activity of lycopene (Liu et al. 2022). Water-in-oil-in-water (W/O/W) emulsions have also been formed using protein–polysaccharide conjugates. In this case, lipophilic bioactive substances can be located in the oil phase, whereas hydrophilic ones can be located in the internal or external aqueous phases (Han et al. 2022).

Delivery systems are also developed to improve the viability of probiotics in foods, protect them during gastrointestinal passage, and release them in the colon (Eratte et al. 2018). For instance, protein-based complexes and conjugates have been used to form W/O/W emulsions that can encapsulate and protect probiotics (Qin et al. 2021b, M. Zhao et al. 2020). The researchers included sodium alginate and calcium–EDTA complexes in the external aqueous phase and *Lactobacillus plantarum* in the internal aqueous phase. The W/O/W emulsions were stabilized by whey protein–EGCG conjugates. When the pH was below 4, the calcium ions dissociated from the calcium–EDTA complexes and then combined with the alginate to form calcium alginate hydrogels. When the pH was above 4, the calcium ions were removed from the calcium alginate gels and chelated with the EDTA, which caused the system to become fluid. This pH-sensitive W/O/W double emulsion has the potential to be used as a colon-targeted delivery system for probiotics (Qin et al. 2021b).

5.4. Texture Modification and Reduced-Fat Products

Protein-based complexes and conjugates can form fluid, semisolid, or solid foods depending on the types and concentrations of proteins, polysaccharides, and/or polyphenols used. Consequently, it is possible to create foods with a wide range of textural attributes using these composite ingredients. They can also be used to manipulate the rheology of emulsions by altering the colloidal interactions between the oil droplets or the textural attributes of the aqueous phase. For instance, researchers have investigated the effects of polysaccharide type and concentration on the rheological properties of emulsions stabilized by OVA–ferulic acid complexes (Huang et al. 2022). The viscoelasticity of the emulsions increased significantly with increasing polysaccharide concentration, which was attributed to the formation of a dense biopolymer network structure in the water

phase. Other researchers reported that high-viscosity O/W emulsions could be produced using complexes of soy proteins and different polysaccharides after heat treatment at 90°C for 30 min (A. Ge et al. 2022). The textural attributes of heat-induced whey protein–*Lycium barbarum* polysaccharide gels have been regulated by altering the pH and amount of polysaccharide added (Z. He et al. 2021). A weak gel structure was formed when the pH was close to the isoelectric point of the proteins. The mechanical strength and fracture stress of gels formed from whey proteins and *Mesona chinensis* polysaccharides were shown to increase with increasing pH (Jiang et al. 2021). Researchers have also shown that the appearance and strength of emulsion gels formed from oppositely charged proteins and polysaccharides can be adjusted by altering the order of the addition of ingredients (Lin et al. 2021).

Recently, the development of structured lipids that mimic the functional attributes of solid fats (which usually contain high levels of saturated and *trans* fatty acids) has received considerable attention from researchers. Oil-filled hydrogels have been examined for their potential to create low-fat and low-calorie products. In this system, oil droplets can be trapped in a semisolid hydrogel formed from protein-based complexes and/or conjugates (Wijaya et al. 2017). These oil-filled hydrogels mimic some of the desirable functional attributes of solid fats and may therefore be useful for producing healthier food products.

5.5. Food Packaging

Packaging plays an important role in improving the quality, enhancing the safety, and extending the shelf life of foods. There has been great interest in developing biodegradable packaging materials from edible ingredients to replace synthetic plastics. However, individual edible ingredients often do not have appropriate film-forming properties and functional attributes. Consequently, there is interest in combining proteins, polysaccharides, and polyphenols to improve the film's overall quality (Q. Wang et al. 2022). Proteins and polysaccharides can be used to assemble films, whereas polyphenols can be used as preservatives because of their strong antioxidant and antimicrobial properties and as film strengtheners because of their ability to cross-link biopolymers. The physical and functional properties of the films depend on the type and concentration of the proteins and other ingredients used: Films formed from milk proteins tend to be colorless, tasteless, and have good ductility; films formed from whey protein and almond oil have good flexibility and moisture permeability; films formed from bovine gelatin have good water-blocking properties; and films formed from zein have water-blocking, antioxidant, and antibacterial properties (Mihalca et al. 2021).

The performance of biopolymer-based films and coatings can be improved by adding functional additives such as antioxidants or antimicrobials, which may be released slowly during food storage, thereby extending the shelf life of foods (Mihalca et al. 2021). Protein-based complexes and conjugates can be used to incorporate these additives into packaging materials. For instance, antimicrobials (e.g., essential oils, phytochemicals, and bacteriocins) and antioxidants (e.g., ascorbic acid, α-tocopherol, and ferulic acid) can form complexes or conjugates with proteins used to assemble packaging materials (Chen et al. 2021). Studies have shown that active packaging materials containing protein-based complexes and conjugates can preserve meat, vegetables, and fruits because of their antimicrobial and antioxidant effects. For example, multilayer films based on gelatin hydrolysates were shown to have better antioxidant and antibacterial activities than synthetic films, which meant that they were more effective at extending the shelf life of tomato in the package (Jamróz et al. 2022). In another study, a shrimp protein–chitosan film was shown to significantly inhibit water transpiration and pathogen growth on the surface of refrigerated fruits, thereby prolonging the shelf life of strawberries during refrigeration (Hajji et al. 2018).

6. CONCLUSIONS AND OUTLOOK

This review focuses on the development and application of novel colloidal food ingredients composed of proteins, polysaccharides, and/or polyphenols. These ingredients can be formed using physical or chemical interactions between the different kinds of molecules involved. Complexes can be formed using physical interactions, such as hydrophobic, hydrogen-bonding, and electrostatic interactions. Conjugates can be formed using chemical methods such as the Maillard reaction, radical grafting, and enzymatic oxidation. However, the type and concentration of ingredients must be carefully selected and controlled, as must the preparation conditions used to fabricate them. The functional properties of proteins, such as their solubility, emulsifying, foaming, gelling, and antioxidant properties, can often be substantially improved by complexing them or conjugating them with polyphenols and/or polysaccharides. Each component in the colloidal ingredient can bring specific functional attributes, leading to the production of multifunctional food ingredients. For instance, in an antioxidant emulsifier, the proteins may help attach the ingredient to the droplet surfaces, the polysaccharides may increase the resistance of the droplets to aggregation, and the polyphenols may provide antioxidant properties. The protein-based ingredients can be widely used in stabilizing Pickering emulsions and HIPE, controlling lipid digestion, effectively encapsulating bioactive substances and probiotics, modifying food texture, and constructing packaging films.

FUTURE ISSUES

1. The use of plant proteins to replace animal proteins has received considerable attention in the food industry because of their better sustainability and lower environmental impact. In the future, complexes and conjugates prepared from plant proteins should therefore be explored in more detail.
2. A variety of emerging technologies are being applied in the preparation of colloidal food ingredients, including sonication, dynamic high-pressure microfluidization, and microfluidics. The application of these new methods in the preparation of novel ingredients with improved functional attributes should therefore be explored.
3. More detailed information about the molecular, structural, and physicochemical properties of colloidal ingredients is required. Information about the conformational changes, bond types, and reaction mechanisms involved in the formation of complexes and conjugates can be obtained using analytical methods such as chromatography, spectroscopy, mass spectrometry, electrophoresis, calorimetry, microscopy, rheology, and computer simulation methods. Typically, it is necessary to use a combination of these techniques to obtain a more comprehensive understanding of the interactions of proteins with other food components.
4. Further research is required to establish the potential of protein-based complexes and conjugates to fabricate more effective delivery systems for bioactive compounds such as nanoparticles, multiple emulsions, and emulsion gels.
5. Further research is needed to establish the gastrointestinal fate and potential toxicity of different kinds of protein-based complexes and conjugates using in vitro, cell culture, animal, and human models.
6. In the future, it will be important to produce protein-based complexes and conjugates on a large scale using economically viable ingredients and processes. Consequently, more research is required to create these processing operations.

DISCLOSURE STATEMENT

The authors are not aware of any other affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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