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Covalently cross-linked proteins & polysaccharides: Formation, characterisation and potential applications

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ABSTRACT

This review presents recent research conducted on the development of various protein-polysaccharide conjugates, their functional properties and industrial applications. These conjugates are formed by the glycosylation of food proteins with carbohydrates via the Maillard reaction and are capable of improving the functional properties of proteins. The Maillard reaction facilitates covalent bonding between a reducing group of a carbohydrate and an amino group of a protein under controlled conditions of temperature, time, pH, and relative humidity. There is a great deal of interest in modifying the functional properties of proteins and in the use of novel conjugates for various industrial applications. This review discusses various methods and their implications for preparing and characterising these conjugates. Furthermore, the physicochemical properties of conjugates such as solubility, thermal stability, emulsifying activity, emulsion stabilising properties, gelling and foaming properties are also analysed. A novel processing technology, a spinning disc reactor, could be an alternative process for the production of protein–polysaccharide conjugates, with desirable functionality in different food systems.

1. Introduction

Proteins are important food ingredients due to their provision of the essential amino acids that are not synthesised in the human body, despite these being necessary for cellular metabolism. Proteins are amphiphilic molecules, which are able to adsorb strongly at the oil–water interface as highly effective emulsifiers. They are commonly used in the food industry in the stabilisation of oil-in-water emulsions [1–3]. However, the functional properties of proteins may be lost under acidic conditions, high ionic strength, high temperature, and the presence of organic solvents, which limits their industrial applications. Thus, if proteins could be converted into more stable forms they could be more versatile in the food industry and elsewhere [4••,5].

Polysaccharides are high-molecule-weight, highly stable, hydrophilic, and biodegradable natural polymers which are usually used as thickeners to modify the viscosity of the aqueous phase in order to stabilise emulsions. Generally, they have little oil–water interfacial activity compared to proteins due to the lack of hydrophobic segments. However, some natural polysaccharides, such as gum arabic (*Acacia senegal*), have emulsifying properties. Gum arabic is a highly branched carbohydrate polymer comprising ~2 wt.% covalently-bonded protein and it is this that is responsible for the surface activity of the gum [6•].

Protein–polysaccharide conjugates are produced via the Maillard reaction, first reported by Maillard in 1912 [7]. It is a series of non-enzymatic browning reactions, which occur naturally between the reducing end of a sugar and an amino acid. We can combine the functional properties of proteins and polysaccharides by covalently linking proteins to polysaccharides via the Maillard reaction to prepare novel protein–polysaccharide conjugates [5,8•,9•,10•]. The covalent bonding between proteins and polysaccharides may be expected to lead to an enhancement of protein functionality both as emulsifiers and stabilisers. The basic mechanism of the coupling is illustrated in Fig. 1 [11••].

High molecular weight glyco-conjugates possess the properties of the protein, strongly adsorbing at the surface of oil droplets and also possess the hydrophilic properties of the polysaccharide, in being highly solvated by the aqueous medium [12]. The conjugation between proteins and polysaccharides provides much more improved steric stabilisation of the emulsion droplets, as illustrated in Fig. 2.

The functional characteristics of proteins can be enhanced by means of physical, chemical or enzymatic treatments to obtain food ingredients for different applications [11••,13]. However, the use of modified proteins as food ingredients, when achieved by chemical methods, is still limited due to some of the chemicals being, or perceived as being, harmful to human health [14–16]. One example is the use of cyanogen bromide to form the ovalbumin–dextran compound that exhibit improved emulsifying properties compared to matrices containing pure ovalbumin [10•]. Thus, the search for naturally occurring chemical reactions remains necessary.

The main advantage of linking proteins to polysaccharides via the Maillard reaction is enhanced solubility and functional properties of

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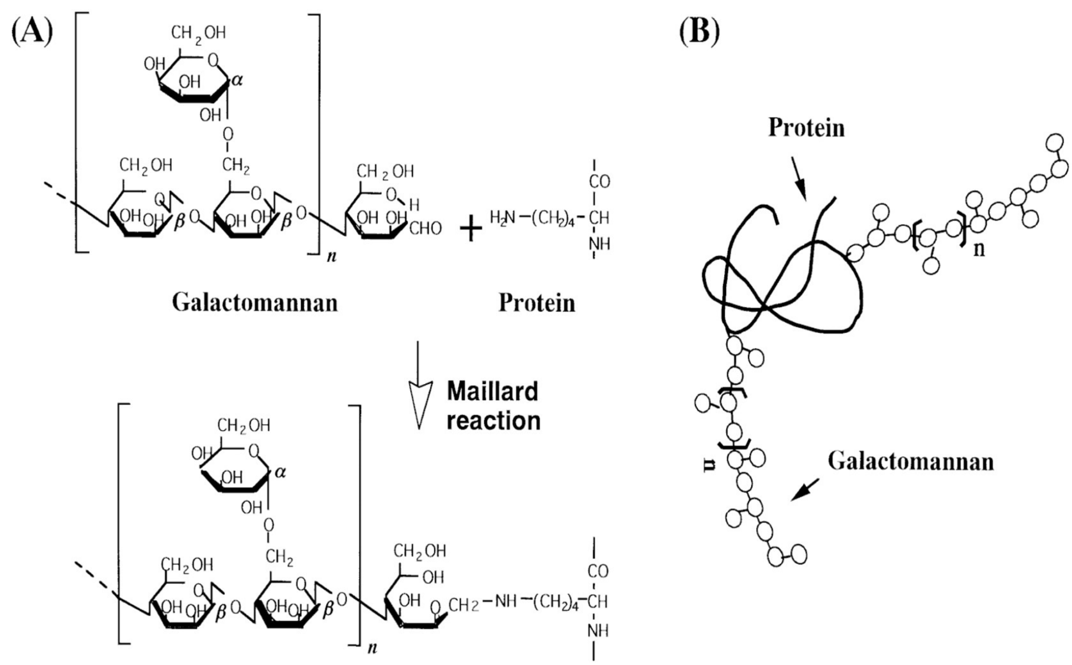

Fig. 1. (A) The basic chemical reaction mechanism for the formation of protein–polysaccharide conjugates via the Maillard reaction. (B) the overview structure of the conjugate. [11••]

proteins over a wide range of environmental conditions, such as low pH and high ionic strength [6•]. For example, gum arabic, a natural glycoprotein, is generally used in the emulsification of citrus flavoured oil for soft drink applications. It has been suggested that gum arabic could be replaced by whey protein–maltodextrin conjugates as the emulsifier and stabiliser instead [9•]. Well-prepared protein–polysaccharide conjugates can show substantial improvement in emulsifying and stabilising properties compared to native proteins, under both low and neutral pH conditions and with colouring agents. Furthermore, the conjugates exhibited effective stabilisation of emulsions over several weeks even after extensive emulsion dilution [9•]. Recently, a comprehensive critical review has been published on food protein–polysaccharide conjugates obtained via the Maillard reaction [17]. The review discusses various stages of the Maillard reaction and the products formed at each stage.

As shown in Fig. 2, the conjugate-stabilised emulsion droplets have a thicker stabilising layer than protein-stabilised emulsion droplets, when the molecular weight of polysaccharide moiety is sufficiently large. In other words, the molecular weight of the polysaccharide determines the thickness of the steric stabilising layer.

2. Preparation of protein–polysaccharide conjugates

Proteins used as functional ingredients in foods are derived mainly from animal products, e.g., meat, eggs and milk, but plant proteins are increasingly used, e.g., from soy protein and peas. Similarly, most research in preparing protein–polysaccharide conjugates has been done on animal-derived proteins (caseins, whey, egg white) [18–20], though there have been some investigations on conjugates derived from plant-based proteins [21–23].

In the case of polysaccharides, dextran and maltodextrin have been most commonly used for preparing these conjugates [18,24,25] while other saccharides have also been investigated such as glucose, lactose and chitosan [21,26,27].

Over the last 25 years, both dry and wet-heating methods have been used for developing protein–polysaccharide conjugates. In 1990, ovalbumin–dextran conjugates were prepared under controlled dry-heating method by a group of Japanese researchers [20]. Two years later, a similar method was adopted to synthesise hybrids between three different proteins (11S globulin *icia faba*, bovine serum albumin, β-casein) and dextran in the Procter Department of Food Science,

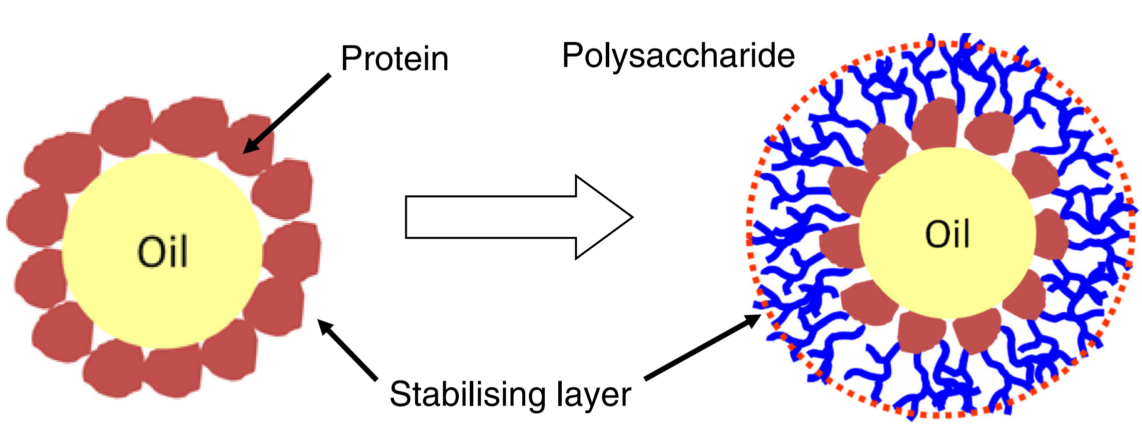

Fig. 2. Comparison between protein- and conjugate-stabilised oil droplets in O/W system. The red blocks represent proteins; the blue branches represent polysaccharides.