ISSN 2347-4289

Stabilizing Food Emulsions By Protein–Polysaccharide Conjugates Of Maillard Reaction-A Review

Habtamu Admassu, Wei Zhao, Ruijin Yang, Mohammed A.A. Gasmalla, ELmuez Alsir

Dept. of Food process Engineering, Addis Ababa Science and Technology University, Addis Ababa, Ethiopia
School of Food science and Technology, Jiangnan University, Wuxi, P.R.China.
Dept. of Nutrition and Food technology, Faculty of Science and Technology,
Omdurman Islamic University, P.O. Box 382, 14415, Khartoum, Sudan

Abstract: Emulsion stability and emulsifying ability are two important factors in the food industry. Emulsions are thermodynamically unstable systems & surfactant must be present to stabilize the system. Proteins are widely used as emulsifiers in the food industry due to their interfacial structure. However, protein-stabilized emulsions are highly sensitive to environmental stresses such as pH, ionic strength, and temperature & require modification to improve such functional properties. Many efforts have been made to develop new food ingredients with improved functional properties (emulsion Stability). Over the past few years, there has been growing interest in the modification of proteins with sugars & several methods have been reported for the conjugation of proteins with polysaccharides to produce better surfactants for emulsion stabilization. Preparing Protein–polysaccharide conjugates by means of Maillard reaction is widely used among those methods. Therefore, this review is focus on maillard conjugates of protein-polysaccharides to stabilize food emulsions.

Key words: Emulsion stability, Protein-Polysaccharide Conjugate, Maillard reaction

1. Introduction

Most food products are complex colloidal systems resulting from the combination of numerous food components (e.g., proteins, carbohydrates, and lipids) organized and arranged in very complex internal microstructures with various types of assemblies such as dispersions, emulsions, foams, gels, etc. The overall stability and structural properties of colloidal systems depends not only on the functional properties of the individual ingredients, but also on the nature and strength of the interactions between them [1]. An emulsion can be defined as a material that consists of small spherical droplets of one liquid dispersed in another liquid in which it is at least partly immiscible. The material within the emulsion droplets is usually referred to as the dispersed, internal, or discontinuous phase, whereas the material that makes up the surrounding liquid is usually referred to as the continuous or external phase[1], [2].

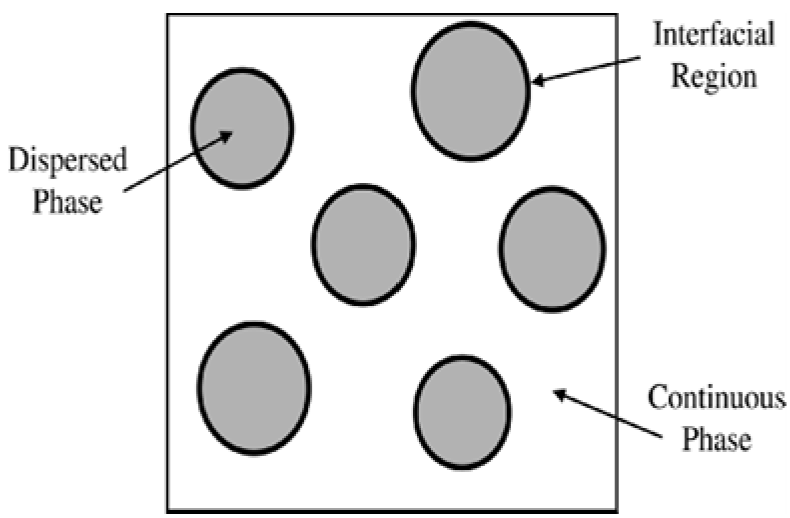


Figure 1: *Schematic illustration of a dispersed system that consists of two fully or partially immiscible liquids. The dispersed phase is surrounded by molecules of the continuous phase, and the two phases are separated by an interfacial region.*

The food industry is one of many industries that heavily rely on the use of emulsions and emulsifiers. Emulsions play an important role in the formulation of foods; some food emulsions (salad dressings, mayonnaise, cream liqueurs, etc) are end products themselves. Food emulsions can also be ingredients which participate in the formation of more complex products such as yoghurts, ice creams and whipped products [3]. From a physiochemical point of view, emulsions are thermodynamically unstable systems, can rapidly or slowly separate into two immiscible phases, over a period of time. The most common processes of emulsion destabilization are droplet-droplet coalescence, flocculation, creaming, and Ostwald ripening. Aggregation of droplets greatly influences shelf life and texture of emulsions [3].

ISSN 2347-4289

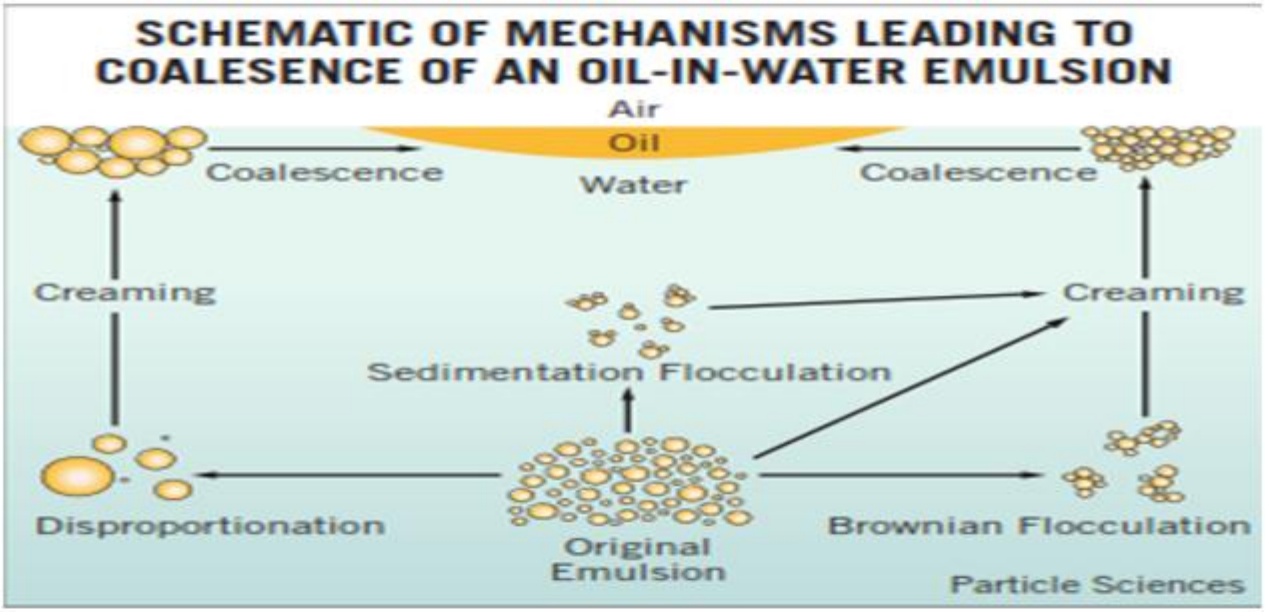


***Figure 2**: Schematic of Mechanisms Leading to Coalescence of an Oil-in-Water Emulsion (Particle Science and Drug development Service) [4]*

2. Emulsion Stabilization

Emulsion stability refers to the ability of an emulsion to resist changes in its properties over time: the more stable the emulsion, the more slowly its properties change. The perceived quality of emulsion based food products is strongly influenced by their stability, rheology and appearance[3] . For a dispersion of one liquid in another to be stable enough to be classified as an emulsion, a third component, such as a surfactant, must be present to stabilize the system. Fine solid particles such as silica beads can also stabilize emulsions if they attach at the interface between the oil and the water to prevent droplets from coalescing [5]. For stabilization of emulsions and suspensions against flocculation, coalescence and Ostwald ripening the following criteria must be satisfied: (i) Complete coverage of the droplets or particles by the surfactant. Any bare patches may result in flocculation as a result of van der Waals attraction or bridging. (ii) Strong adsorption (or ‘’anchoring’’) of the surfactant molecule to the surface of droplet or particle. (iii) Strong solvation (hydration) of the stabilizing chain to provide effective steric stabilization, (iV) Reasonably thick adsorbed layer to prevent weak flocculation. Most of the above criteria for stability are best served by using a polymeric surfactant [6]. Proteins, especially caseins and whey proteins are widely used as emulsifiers in food, cosmetic and pharmaceutical industries for many years in the stabilisation of oil-in-water emulsions [7],[8],[9],[10] . The efficiency of these emulsifiers is a function of their interfacial structure [10]. They have amphiphilic (hydrophobic and hydrophilic) characteristics and as such are able to adsorb strongly at the oil–water interface. The adsorbed protein molecules are responsible for reducing the surface tension and able to stabilise emulsions by preventing droplet aggregation and coalescence through electrostatic and/or steric repulsive forces [7], [8], [9]. However, protein-stabilized emulsions are highly sensitive to environmental stresses such as pH, ionic strength, and temperature. When the pH approaches the isoelectric point of the protein and/or the salt concentration is higher in the emulsion, the electrostatic repulsion of the protein adsorption layers decreases, and therefore coalescence and creaming happen. When emulsion is subjected to heat treatment, for pasteurization or sterilization purposes, aggregation happens because of the denaturation of the protein that holds the droplets together [7], [8]. Many food proteins require modification to improve such functional properties as solubility, foaming and emulsifying activity. Functional properties of proteins are closely related to their size, structural conformation, and level and distribution of ionic charges. Mostly, the three dimensional structure of the protein molecule decides the physicochemical functions of the proteins [11].

ISSN 2347-4289

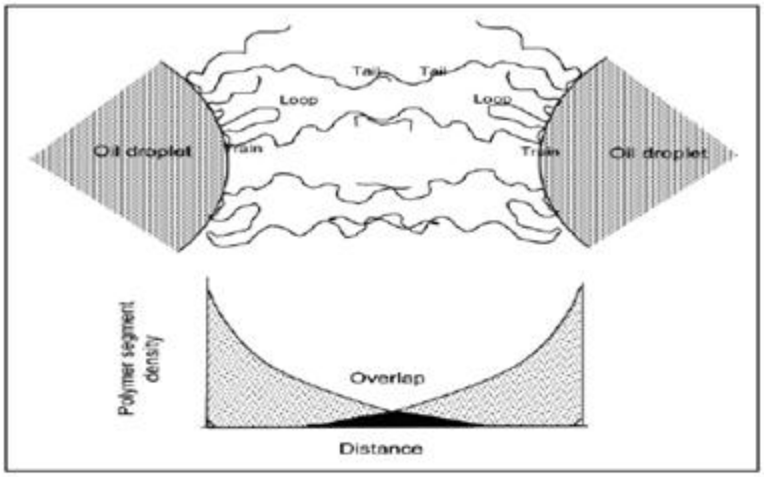


Figure3: *Schematics of steric repulsion between adsorbed protein layers at the oil-water interface of emulsion droplets [12] Chemical treatments that could cause alteration of these properties include reactions that either introduce a new functional group to the protein or remove a component part from the protein [13].*

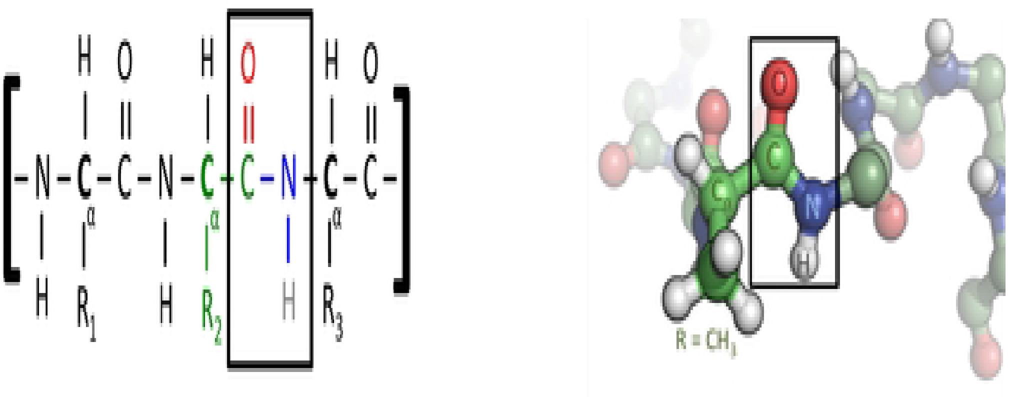


Figure: *Three-dimensional structure of a peptide bond between an alanine and an adjacent amino acid (left) & Chemical structure of the peptide bond (right) [11]*

To improve functional properties of proteins including their emulsifying ability, chemical modifications have often been made [14]. Some researchers have found that protein-polysaccharide conjugates as the emulsifying agent rather than the protein alone can markedly enhance emulsion stabilisation. In recent years, polysaccharides are widely used for stabilisation of food emulsions and foams. High molecular weight emulsifiers such as gum arabic, casein, dextran, modified starch, and others, are often used as ingredients to stabilise oil-in-water food emulsions [15]. Generally, there are three classes of complexes namely; (a) naturally-occurring complexes in which protein residues are covalently attached to the polysaccharide chains as is the case, for example, with gum Arabic; (b) Maillard conjugates, which are formed by interaction of the reducing end of a polysaccharide with an amine group on a protein forming a covalent bond; and (c) electrostatic complexes formed between a polysaccharide and a protein with opposite net charge [8]. However, this review only focuses on Maillard conjugates.

3. Development of Protein – polysaccharide Conjugate & Maillard reaction

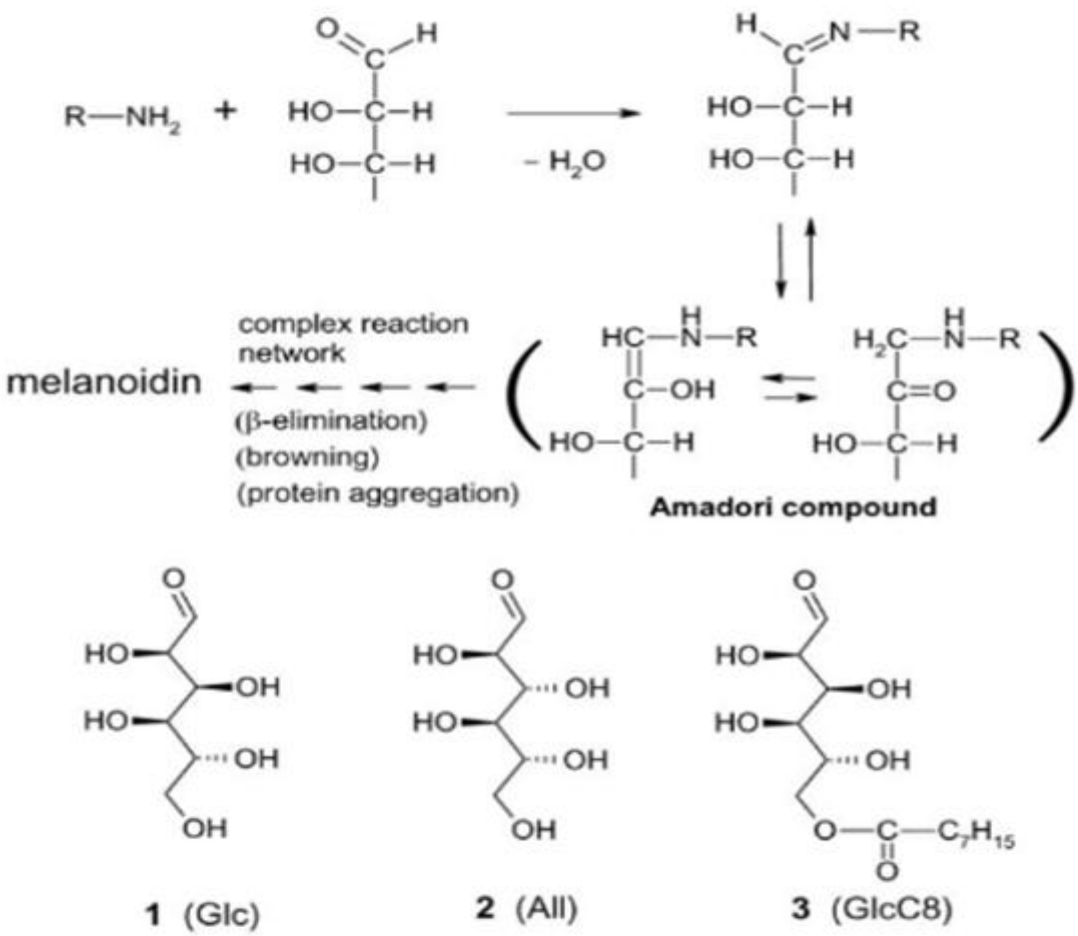
Many efforts have been made to develop new food ingredients with improved functional properties [16], [17] (1,2). Over the past few years, there has been growing interest in the modification of proteins with sugars [14] (3) & several methods have been reported for the conjugation of proteins with polysaccharides to produce better surfactants for emulsion stabilization[16] (1). Preparing Protein–polysaccharide conjugates by means of Maillard reaction is widely used among those methods [18], [19],[20] . Maillard reaction is a spontaneous and naturally occurring reaction, which involves a complex network of non-enzymatic reactions resulting from the initial condensation between an available amino group and a carbonyl-containing moiety (between reducing sugars and protein amino groups) , in certain conditions of temperature and water activity[17],[18], [21]. The non-enzymatic maillard reaction products(MRPs) formed during processing, packaging and storage via amino and carbonyl compounds interactions are common to many food systems, and several authors proved that these MRPs have antioxidant activity and they can act as radical scavengers and metal chelators, thus potentially providing more than one mechanism of action to prevent lipid

ISSN 2347-4289

oxidation[22] (4). Different kinds of proteins have been modified in this method. Glucose, glucose 6-phosphate and dextran were separately conjugated to improve the emulsifying properties of ovalbumin , 6- phosphate and galactomannan were used to make better applications of both egg protein and whey proteins, galactomannan improved emulsifying properties of protamine, it was also discovered that the product of glycosylation of rice endosperm protein had better solubility and emulsifying properties than those of enzymic hydrolysis and original proteins [18]. Protein–polysaccharide conjugates have used as useful new biopolymers with excellent functional properties, e.g. protein solubility and emulsifying properties. In general, the functionalities of proteins are not increased by mere coexistence with polysaccharides but by conjugation, which is based on Maillard-type reactions between the amino groups of proteins and the reducing-end carbonyl groups of polysaccharides. Compared with mono- or disaccharides, conjugation of polysaccharides with proteins has led to significant improvements in the physical and/or chemical properties of the latter, e.g. providing an ideal combination of the good emulsifying properties of proteins and the stabilising ability of polysaccharides [16] ,[23].

4. Mechanism of conjugation

The early stage of Maillard reaction involves a condensation between the carbonyl group of a reducing carbohydrate with an available, unprotonated amino group, mainly the Ɛ-amino group of the Lys residues in proteins. With aldoses, such as glucose, this leads to a Schiff base with the release of water. The Schiff base subsequently cyclises to the corresponding N-glycosylamine, which then undergoes an irreversible Amadori rearrangement to produce the Amadori compound. The intermediate stage begins with the degradation of the Amadori product following various divergent pathways to give a large multiplicity of poorly characterised compounds. In the final stage, highly coloured, insoluble, nitrogen-containing polymeric compounds, referred to as melanoidins, are formed. Ideally, to produce a glycoconjugate destined for incorporation into food, Maillard reaction needs to be performed under carefully controlled conditions to prevent the later stage changes [14],[17] [20].



***Example** of Bovine serum albumin-sugar conjugates through* the *maillard reaction [14]*

ISSN 2347-4289

The high molecular weight glyco-conjugate is supposed to combine the properties of a hydrophobic protein, being firmly attached to the oil droplet surface, with the property of a hydrophilic polysaccharide, being highly solvated by the aqueous phase medium. The complexation between proteins and polysaccharides at the emulsion droplet surface can improve steric stabilization. Droplet size can be smaller if the polysaccharide is present during homogenization and rate of creaming may be reduced so long as there is no bridging flocculation [24].

5. Conclusion

Covalent linkage of the Protein – Polysaccharide through non-chemical means such as the Maillard reaction, produces high molecular weight biopolymers known as glycoconjugates. Creation of glycoconjugates is often achieved through conjugation or attachment of a suitable carbohydrate to a particular binding site on the protein. Many of the positive benefits of producing Maillard generated conjugates include improvements in emulsifying activity, foaming properties, calcium complexing, solubility, and heat stability. Emulsion stability enhanced by the use of glycoconjugates can prevent aggregate formation which in turn prevents flocculation and coalescence, processes that can negatively lead to creaming.

Reference

[1] Amid, B. T., Mirhosseini, H., Poorazarang, H., & Mortazavi, S. A. (2013). Implications of partial conjugation of whey protein isolate to durian seed gum through Maillard reactions: foaming properties, water holding capacity and interfacial activity. Molecules, 18(12), 15110-15125.

[2] Batista, A. P., Raymundo, A., Sousa, I., Empis, J., & Franco, J. M. (2006). Colored Food Emulsions—Implications of Pigment Addition on the Rheological Behavior and Microstructure. Food Biophysics, 1(4), 216-227.

[3] Chen, W., Li, X., Rahman, M. R. T., Al-Hajj, N. Q. M., Dey, K. C., & Raqib, S. M. (2014). Emulsification properties of soy bean protein. Nusantara Bioscience, 6(2).

[4] Chobert, J.-M. (2012). Milk protein tailoring to improve functional and biological properties. J. BioSci. Biotech. 1(3): 171-197.

[5] DAMODARAN, S. (2005). Protein Stabilization of Emulsions and Foams. JOURNAL OF FOOD SCIENCE—Vol. 70, Nr. 3,.

[6] orobantu, L. S., Yeung, A. K., Foght, J. M., & Gray, M. R. (2004). Stabilization of oil-water emulsions by hydrophobic bacteria. Appl Environ Microbiol, 70(10), 6333-6336.

[7] Evans, M., Ratcliffe, I., & Williams, P. A. (2013). Emulsion stabilisation using polysaccharide–protein complexes. Current Opinion in Colloid & Interface Science, 18(4), 272-282.

[8] Fernández, C. L., Doval, M. M., Romero, A. M., & Judis, M. A. (2014). Maillard Reaction Product from Bovine Plasma Proteins as Antioxidant on Model Systems. International Journal of Applied Science and Technology volume, 4 No. 5.

[9] Gerber, H.-P., Senter, P. D., & Grewal, I. S. (2014). Antibody drug-conjugates targeting the tumor vasculature. mAbs, 1(3), 247-253.

[10] Jiménez-Castaño, L., Villamiel, M., & López-Fandiño, R. (2007). Glycosylation of individual whey proteins by Maillard reaction using dextran of different molecular mass. Food Hydrocolloids, 21(3), 433-443.

[11] Kasran, M. (2013). Development of Protein Polysaccharide Complex for Stabilization of Oil-in-Water Emulsions. A Thesis presented to The University of Guelph.

[12] Markman, G., & Livney, Y. D. (2012). Maillard-conjugate based core-shell co-assemblies for nanoencapsulation of hydrophobic nutraceuticals in clear beverages. Food Funct, 3(3), 262-270.

[13] Martinez-Alvarenga, M. S., Martinez-Rodriguez, E. Y., Garcia-Amezquita, L. E., Olivas, G. I., Zamudio-Flores, P. B., Acosta-Muniz, C. H., & Sepulveda, D. R. (2014). Effect of Maillard reaction conditions on the degree of glycation and functional properties of whey protein isolate – Maltodextrin conjugates. Food Hydrocolloids, 38, 110-118.

[14] McClements , D. J., & Weiss , J. (2005). Lipid Emulsion. Bailey's Industrial Oil and Fat Products , Lipid Emulsion , Sixth Edition, Six Volume Set. Chapter - 14, Fereidoon Shahidi(Editer). John Wiley & Sons, Inc.

[15] MU, L., ZHAO, H., ZHAO, M., CUI, C., & LIU, L. (2011). Physicochemical Properties of Soy Protein Isolates-Acacia Gum Conjugates. Czech J. Food Sci.Vol. 29, No. 2: 129–136.

[16] Service, P. S. D. D. (2011). Emulsion Stability and Testing. Technical Brief , Volume 2.

[17] Spotti, M. J., Martinez, M. J., Pilosof, A. M. R., Candioti, M., Rubiolo, A. C., & Carrara, C. R. (2014a). Influence of Maillard conjugation on structural characteristics and rheological properties of whey protein/dextran systems. Food Hydrocolloids, 39, 223-230.

[18] Spotti, M. J., Martinez, M. J., Pilosof, A. M. R., Candioti, M., Rubiolo, A. C., & Carrara, C. R. (2014b). Rheological properties of whey protein and dextran conjugates at different reaction times. Food Hydrocolloids, 38, 76-84.

[19] Tadros, T. (2009). Polymeric surfactants in disperse systems. Adv Colloid Interface Sci, 147-148, 281-299.

ISSN 2347-4289

[20] Traynor, M. P., Burke, R., Frías, J. M., Gaston, E. a., & Barry-Ryan, C. (2013). Formation and stability of an oil in water emulsion containing lecithin, xanthan gum and sunflower oil. International Food Research Journal, 20(5)2173-2181

[21] Wooster, T. J., & Augustin, M. A. (2006). Beta-lactoglobulin-dextran Maillard conjugates: their effect on interfacial thickness and emulsion stability. J Colloid Interface Sci, 303(2), 564-572.

[22] Xu, K., & Yao, P. (2009). Stable oil-in-water emulsions prepared from soy protein-dextran conjugates. Langmuir, 25(17), 9714-9720.

[23] Zheng, Z., Luo, Y., Yao, L., Lu, J., & Bu, G. (2014). Effects of Maillard reaction conditions on the functional properties of WPI chitosan oligosaccharide conjugates. J Food Sci Technol, 51(12), 3794-3802.

[24] Zhuo, X. Y., Qi, J. R., Yin, S. W., Yang, X. Q., Zhu, J. H., & Huang, L. X. (2013). Formation of soy protein isolate-dextran conjugates by moderate Maillard reaction in macromolecular crowding conditions. J Sci Food Agric, 93(2), 316-323.