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Outputs through the collaborative works with Prof. G. O. Phillips on hydrocolloid emulsifiers

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A B S T R A C T

Some natural hydrocolloids exhibit emulsifying properties (emulsifying activity and emulsion stabilizing ability), and carbohydrate with proteinaceous moiety generally plays an essential role in the O/W emusltions. Although the proteinaceous moiety is a minority in the whole hydrocolloid, it can activate the interface between oil and water by adsorbing onto the interface due its amphipathic character. Thus, protein is not just a contamination but works as a functional ingredient. On the other hand, carbohydrate bound to the proteinaceous moiety contributes to emulsion stability through steric effect by forming hydrated layer around the surface of oil droplets. In this review, gum arabic, gum ghatti, and sugar beet pectin are focused, and findings on their emulsification mechanisms and the solutions for improved functionality and reduced natural diversity of these hydrocolloids are summarized as outputs from the collaborative works with Prof. G. O. Phillips for more than 10 years.

1. Introduction

Glyn O. Phillips Hydrocolloids Research Centre (PHRC) was established in June 2003 as a base for collaboration between San-Ei Gen F. F. I., Inc (Osaka, Japan) and an academic centre in Glyndwr University (formely NEWI) (Wales, UK). This was a unique framework of the university-industry collaboration, and as a result of extensive joint programs, not only publications but also commercial products have been emerged successfully. As a series of collaborative activities, international forum was organized three times in 2005, 2007, and 2009 by inviting experts throughout the world in specific subjects of research interest, which was aimed to elicit new thinking and promote the collaboration. One of the main subjects of the forum was structure and functionality of natural hydrocolloids, particularly polysaccharides with emulsifying properties. This subject was and still is a challenge, which starts from acceptance of the diversity and variety of nature to how we can reduce them to meet with industrial usage and consumers' benefits. In this article, outputs from the collaboration with Prof. Phillips are presented in a review form in the following research subjects; 1. gum arabic, 2. gum ghatti, and 3. sugar beet pectin.

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2. Gum arabic

Gum arabic, particularly form *Acacia senegal* species, has been serving in the industry as one of the best hydrocolloid emulsifiers. Thus, researches have been carried out for elucidation of emulsification mechanism of the gum with focusing on the role of the active component; the arabinogalactan protein fraction. In accordance with this background, the title of the 1st forum in 2005 was "The Structure and Function of Arabinogalactan Proteins (AGPs)", followed by the 2nd forum in 2007 entitled "Natural Hydrocolloid Emulsifiers". These were very systematic and well organized conferences limited to the PHRC family, and papers covered wide range of related subjects from biological to industrial importance.

Gum arabic is believed to contain three distinct fractions, including glycoprotein (GP), arabinogalactan (AG), and AGP in increasing order of average molecular weight, and all these fractions consist of heterogeneous and highly branched carbohydrate structure with different protein contents (Williams & Phillips, 2009). The AGP fraction plays an essential role in emulsification (Randall, Phillips, & Williams, 1988) with emphasis placed on the presence of small amount of protein in the fraction (~2% in the whole gum) (Randall, Phillips, & Williams, 1989). This is supported by the loss of emulsifying properties (Randall et al., 1988) and interfacial elasticity (Elmanana, Al-Assaf, Phillips, & Williams, 2008) for the gum treated with protease. The AGP molecule has a molecular mass of 1–2 × 10^6 g/mol and consists of a peptide chain possibly containing ~250 amino acids with short arabinose side chains and much larger carbohydrate blocks of molecular mass ~4.0 × 10^4 g/mol (Mahendran, Williams, Phillips, Al-Assaf, & Baldwin, 2008). Also, health benefits of the gum in human have been indicated, including not only prebiotic effects resulting from the production of short-chain fatty acids by colon fermentation but also the reduction of blood pressure in patients with diabetic nephropathy (Phillips & Phillips, 2011). In both cases, AGP is a bioactive component.

Determination of AGP content using size exclusion chromatography coupled with multi-angle laser light scattering has been established as a method for quality control of the gum as a hydrocolloid emulsifier (Al-Assaf, Katayama, Phillips, Sasaki, & Williams, 2003), and the amount of AGP is of particular importance (Al-Assaf et al., 2008). In relation, agglomeration of the proteinaceous components occurs during maturation process, which not only increases the molecular weight of the gum but also modifies the surface properties of the molecules in a way that they are more prone to agglomeration (Cui, Wang, Phillips, Blackwell, & Nikiforuk, 2006). Thus, function of protein as a molecular linker can be emphasized.

It is indicated from the relationship between emulsion stability and the molecular properties of the oil adsorbed component of gum arabic that the higher the molecular weight of the adsorbed component, the higher is the emulsion stability (Katayama et al., 2006). High pressure homogenization exerts good emulsification performance, particularly when gum arabic of high molecular-weight is used (Sakata et al., 2006). High pressure homogenization is necessary for unfolding of the aggregation of AGP to make it accessible at the interface of emulsions, and large AGP molecules can adsorb extensively with the oil droplets and would be thermodynamically more stable than the small molecules (Aoki et al., 2007b). Emulsion stability is related not only to the amount of adsorbed component but also to the conformational changes induced by the pressure treatment (Sakata et al., 2006). Thus, it is important to consider the combination with processing condition for the best usage of the gum.

The industry may have suffered from the variation of quality for naturally occurring gum, which can be caused by harvest region/season/year and production batch. The new form of *Acacia senegal*; Acacia (*sen*) SUPER GUM™ is characterized by its precisely structured molecular dimensions with improved and constant emulsifying properties (Al-Assaf, Phillips, Aoki, & Sasaki, 2007). This can be set as a new generation of gum arabic and in strategic position commercially. The controlling factor of this material is the agglomeration of the proteinaceous components through the maturation process without any chemical changes, and as a result, the amount of the AGP fraction is increased up to more than double the amount present originally (Al-Assaf et al., 2007). This converts a poor emulsifier into a good one with a dramatic increase in the interfacial properties and coverage of the oil droplets in emulsion. The maturation process is comparable to aging when the gum is stored naturally after collection. As the Acacia tree grows, the molecular weight of the gum increases from 320,000 (at 5 years) to a maximum of 790,000 (after 15 years), and the amount of the AGP fraction also increases with the age of the tree (Idris, Williams, & Phillips, 1998). As average molecular weight of Acacia (*sen*) SUPER GUM™, ca. 2.0 × 10^6 g/mol has been reported (Aoki, Al-Assaf, Katayama, & Phillips, 2007a) compared to standard gum arbic in variation; ~8.0 × 10^5 g/mol (Al-Assaf et al., 2008).

In a series of international cross studies using Acacia (*sen*) SUPER GUM™, mechanism of the maturation process is deduced (Fig. 1) as the transfer of protein associated with the lower molecular weight components to give larger concentrations of AGP which also occurs naturally (Aoki et al., 2007a). Through the maturation process, no profound structural changes occur in the gum as a whole, which is supported by an immunological

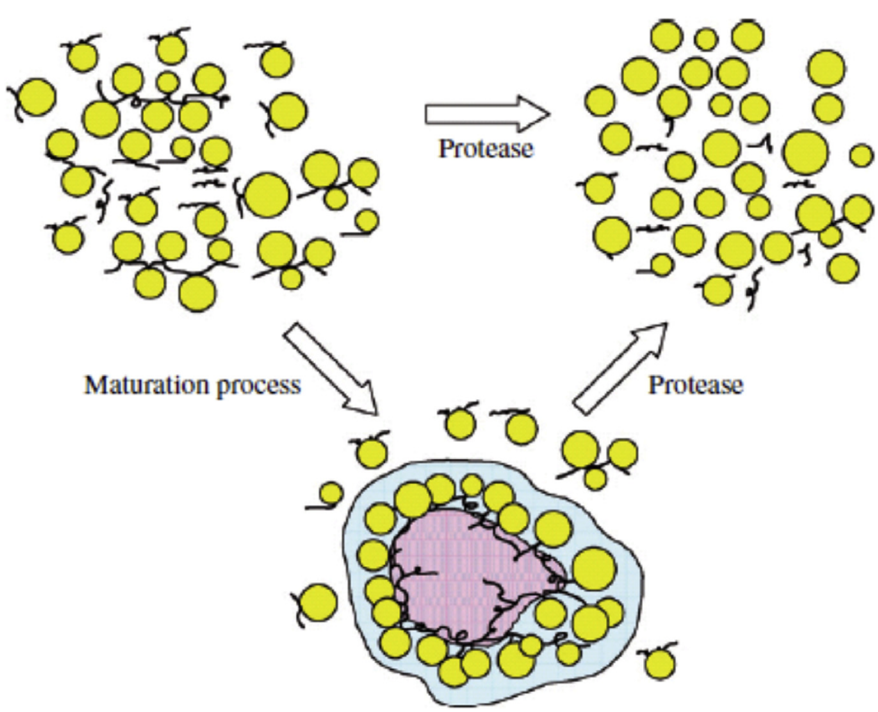

Fig. 1. Maturation process and protease treatment of gum arabic. AGP formed by the maturation process behaves identically with that present in the control gum and retains the polypeptide linkage as in the control. AGP in the processed gum can be hydrolyzed by the protease enzyme in exactly the same way as the AGP in the control gum. Cited from Aoki et al. (2007a).

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