Food Hydrocolloids xxx (2016) 1–7

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Characterization and emulsifying properties of octenyl succinate anhydride modified *Acacia seyal* gum (gum arabic)

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ARTICLE INFO

Article history:
Received 19 July 2016
Received in revised form
1 October 2016
Accepted 14 October 2016
Available online xxx

Keywords:
Gum arabic
Acacia seyal gum
Octenyl succinate anhydride
Structure characterization
Emulsifying properties

ABSTRACT

This study aimed to investigate the structure characterization and emulsifying properties of esterified *Acacia seyal* gum (gum arabic) with various octenyl succinate anhydride (OSA) contents (0, 1%, 2%, and 3% based on the weight of *Acacia seyal* gum) at different OSA incorporates (%OS, 0, 0.64, 1.09, 1.80). Fourier transform infrared spectroscopy and ^{1}H NMR spectroscopy revealed that OSA groups were introduced into the *Acacia seyal* gum (AS) molecular structure and possibly substituted the rhamnopyranosyl of AS. Static light scattering analysis showed that the molecular weight of OSA-modified AS (OS-AS) significantly increased. Meanwhile, the crystallinity of AS and OS-AS demonstrated no significant difference. In addition, rheological results revealed that the apparent viscosity of OS-AS was higher than that of AS and increased with increasing %OS. The emulsion activity of OS-AS increased nearly twice those of the original AS and its emulsion stability were also significantly improved. Results indicate that the OS-AS have potential applications for microencapsulation and emulsions that require long-term stability.

1. Introduction

Gum arabic (GA) is an exudate from trunks and branches of acacia trees, namely *Acacia senegal* gum and *Acacia seyal* gum (AS), and is a branched, neutral or slightly acidic, complex polysaccharide together with a small amount of structural protein (Randall, Phillips, & Williams, 1988; Renard, Garnier, Lapp, Schmitt, & Sanchez, 2012). In general, the polysaccharides and proteins present in GA are consisted of three mainly fractions, including arabinogalactan (AG), arabinogalactan protein (AGP), and glycoprotein (GP), which differ from their molecular weight and chemical composition (Desplanques, Renou, Grisel, & Malhiac, 2012). The AG fraction which represents about 88% (in weight) of the total gum has a low molecular weight (M_w, ~300 KDa) and associated little protein content of below 1%. The AGP fraction (~10% of the total gum) has a high molecular weight (M_w) (~1500 KDa) and protein content (~10%). The GP fraction (<2% of the total gum) has the lowest molecular weight (M_w, ~250 KDa) and the highest protein content (~20%–50%) (Mahendran, Williams, Phillips, Al-Assaf, & Baldwin, 2008; Randall, Phillips, & Williams, 1989). Among these fractions, AGP is the most interfacially active component (Castellani, Al-Assaf, Axelos, Phillips, & Anton, 2010; Ray, Bird, Iacobucci, & Clark, 1995), and is primarily responsible for the emulsifying properties of GA (Al-Assaf, Phillips, Aoki, & Sasaki, 2007; Randall et al., 1988). This fraction can be adsorbed on the oil-water interface to form a visco-elastic film and reduce the interfacial tension between oil and water because of its amphiphilic characteristics, which is conferred by the hydrophobic protein chains combined to the hydrophilic polysaccharide fragments (Castellani, Al-Assaf et al., 2010; Castellani, Guibert et al., 2010).

Currently, GA has been widely used in the food industry as an emulsifiers (Patel & Goyal, 2015). However, GA is generally required a high concentration of approximately 15%–25% (w/w) to achieve a stable 20% (w/w) oil in-water emulsions since the AG fraction, which represents the bulk of the gum, is not involved in the emulsification process (Leroux, Langendorff, Schick, Vaishnav, & Mazoyer, 2003; Randall et al., 1988, 1989). In addition, the natural

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http://dx.doi.org/10.1016/j.foodhyd.2016.10.043
0268-005X/

variability (geography, soil, age of the tree, and on both species) of GA has became a barrier to complete industrial acceptance (Al-Assaf et al., 2007). Currently, about one-quarters of GA comes from the species AS. But AS is generally less valued than *Acacia senegal* gum due to its poor emulsifying properties (Dickinson, 2003; Fauconnier et al., 2000; Flindt, Al-Assaf, Phillips, & Williams, 2005), it then can neither be used in emulsions that need long term stability (Elmanan, Al-Assaf, Phillips, & Williams, 2008; Siddig, Osman, Al-Assaf, Phillips, & Williams, 2005), nor be used as encapsulating agent for some monoterpenes alone (Bertolini, Siani, & Grosso, 2001). Therefore, improving the emulsifying properties of GA by modification, and researching effects of structure on emulsifying properties of modified gum, especially AS, is urgently needed.

Recently, there has been increasing interest in chemical modification of GA to enhance its emulsifying properties, and this involved esterification using octenyl succinate anhydride (OSA) and dodecenyl succinic anhydride (DSA). Pan, Yang, and Qiu (2015), Sarkar, Gupta, Variyar, Sharma, and Singhal (2013) and Sarkar and Singhal (2011) showed the optimum condition for synthesis of modified GA using OSA, and found that OSA-modified GA had improved performance compared to the original GA. Wang, Williams, and Senan (2014) demonstrated the modified GA (*Acacia senegal* gum) can be readily synthesized in aqueous solutions using DSA, and the modified GA had superior emulsifying properties to GA. However, the structure characterization, emulsifying properties and effects of OSA incorporation (%OS) on functionalities and applications of OSA-modified AS (OS-AS) have not yet been reported.

The present study aimed to enhance the emulsifying properties of AS through chemical modification using different concentrations of OSA. Effects of %OS on the apparent viscosity and emulsifying properties of AS were evaluated. Fourier transform infrared (FT-IR), ^{1}H NMR spectroscopy, static light scattering spectrometer (SLS) and X-ray diffraction (XRD) were employed to compare the influence of OSA-modification on the structure of AS, and to elucidate the possible relationship between the structure and emulsification.

2. Materials and methods

2.1. Materials

Acacia seyal gum (gum Arabic) was obtained from Nexira (Shanghai, China). Octenyl succinate anhydride (OSA) (99.9% purity) was purchased from Vertellus (Shenzhen, China). Evening primrose oil was obtained from Tianjin Baoxin International Oil Bio Co., Ltd. Chromatographic pure acetonitrile and methanol were purchased from TEDIA (Shanghai, China). Spectroscopic pure potassium bromide was obtained from Solarbio (Beijing, China). All other chemicals were analytical reagents and used as received.

2.2. Preparation of OS-AS

Preparation was carried out according to the method of Pan et al. (2015) with some modification. Dry weight AS (30.00 g) was dispersed in deionized water to prepare a 30% (w/v) solution. The pH was adjusted to 8.00 using 0.5 M NaOH solution. Four reactions were performed using 0, 1%, 2%, 3% OSA (W_t % based on the weight of dry AS) respectively, which were diluted with ethanol and added at 25 °C. The mixtures were allowed to reaction at 40 °C for 1.5 h with pH maintained at 8.00. Following, the reactions were ceased by adjusting the pH to 6.00 using 0.1 M HCl solution. OS-AS was obtained by spray drying. Then the product was dispersed in deionized water to prepare a 10% (w/v) solution following by washing with absolute ethanol to remove the residue of OSA. This process was repeated for 5 times. The final solid portion was oven-dried at 40 °C for 24 h. The products are referred to as AS0, AS1, AS2 and AS3 corresponding to 0, 1%, 2% and 3% OSA (W_t % based on the weight of dry AS), respectively.

2.3. Fourier-transform infrared spectroscopy (FT-IR)

The changes in chemical structure of AS and OS-AS were qualitatively analyzed using FT-IR (Nicolet 380, Thermo Nicolet, USA). Samples were prepared by grinding the finely powdered samples with potassium bromide (KBr). The spectrum was recorded over the wave number range of 400–4000 cm^{-1}. The samples were dried at 105 °C for 12 h before analysis to avoid the interference of moisture.

2.4. Determination of bound %OS content

The bound OS content was determined according to Qiu, Bai, and Shi (2012) with some modifications. Exactly, 0.5000 g dry samples were immersed in 10 mL of 4 M NaOH, and stirred overnight. The alkali treated solutions (2 mL) were transferred into a 25 mL volumetric flask, mixed with 18 mL of 1 M HCl and made volume to 25 mL with acetonitrile. The solutions were then analyzed using an HPLC system (D-2000 HSM, HITACHI, Tokyo, Japan) with a Nova-Pak® C18 column (4 μm, 3.9 × 150 mm, Waters, CA, USA), using a mixture of acetonitrile and water containing 0.1% formic acid (35:65, v/v) as the mobile phase. 10 μL of solution was injected after filtered through 0.45 μm membrane, the UV spectra was recorded at 200 nm. The OS content was calculated from the standard curve (y=19.369×−0.0662) of OSA plotted using OSA concentration (μg/mL) vs total peak area. The bound %OS of OS-AS were calculated by using following equation:

$$\%OS = \frac{12500W_t}{W}$$

where W is the dry weight (g) of OS-AS, W_t is the OS content calculated from standard curve, 12,500 is dilution factors.

2.5. ^{1}H NMR experiment

^{1}H NMR experiment of AS and OS-AS was carried out according to Nie et al. (2013) with slight modifications. Both samples were dissolved in 0.5 mL deuterium oxide (D_2O) (~2%, w/v), and deuterium exchanged by successive freeze-drying steps. The samples were kept in D_2O at room temperature for 3 h before NMR analysis. ^{1}H NMR spectrum was recorded on NMR spectrometer (Avance 600 MHz, Brucker, Rheinstetten, Germany) at 25 °C.

2.6. Determination of molecular weight

Molecular weight of AS and OS-AS was determined using an laser light scattering spectrometer (BI-200SM, Brookhaven Instruments, New York, USA) with He-Ne laser (633 nm) as the light source according to Wang, Burchard, Cui, Huang, and Phillips (2008) and Wang, Huang, Nakamura, Burchard, and Hallett (2005) with slight modifications. Static light scattering measurements of the samples were performed at 25 °C. The stock gum solutions (5 mg/mL) used for molecular weight measurement were prepared with 0.2 M NaCl. The scattering angles detected ranged from 20° to 150° in steps of 10°. A specific refractive index increment was set at 0.141 mL/g.

Please cite this article in press as: Shi, Y., et al., Characterization and emulsifying properties of octenyl succinate anhydride modified *Acacia seyal* gum (gum arabic), *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.10.043