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Preparation and stabilizing behavior of octenyl succinic esters of soybean soluble polysaccharide in acidified milk beverages

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ABSTRACT

Soybean soluble polysaccharide (SSPS) is anionic polysaccharide extracted from the by-product of isolated soy protein production. In this study, a simple and eco-friendly procedure had been developed to prepare high-molecular-weight octenyl succinic esters of SSPS (OSA-SSPS) via the esterification between SSPS and octenyl succinic anhydride (OSA). The absolute molecular weights of OSA-SSPS and SSPS were 620 kDa and 53 kDa, respectively. OSA-SSPS had some similar properties to SSPS, such as microstructure and viscosity of 1 wt% concentration. However, compared to SSPS, OSA-SSPS showed different milk protein stabilization properties. The stabilizing behavior of OSA-SSPS was better than that of SSPS at pH range of 3.8–4.6, and poorer at pH 3.6. The model mixture of OSA-SSPS had smaller particle sizes at pH range of 3.8–4.6 and larger absolute negative charges at pH 2.0–10.0. In addition, from the molecular diameter measured by DLS and AFM image, the surface concentration of OSA-SSPS was larger than that of SSPS, which indicated that the thicker OSA-SSPS layer produces larger steric repulsion to milk protein particles. The mechanism for the greater ability of OSA-SSPS to stabilize milk proteins was proposed on the basis of the results discussed in this research.

1. Introduction

Acidified milk drinks, such as fermented yogurt, are world-wide beverages focusing on human health benefits and for the best taste, these pH ranges from 4.0 to 4.6. Since the milk proteins such as caseins usually aggregate and precipitate under the acidic pH conditions, stabilizers are added to acidified milk drinks (Nakamura, Fujii, Tobe, Adachi, & Hirotsuka, 2012). Although such stabilizers have been ever dominated by a well-known polysaccharide named gum Arabic (GA) from Acacia Senegal, due to the cost and availability constraints, attempts to replace GA by high methoxyl pectin (HM-pectin), SSPS and other polysaccharides or modified starches have been consistently tried (Chivero, Gohtani, Ikeda, & Nakamura, 2014). HM-pectin and SSPS are negatively charged stabilizers, under acidic conditions (pH 3.0–4.6), they can adsorb to the positively charged caseins, thereby generating steric repulsive forces and electrostatic repulsive forces between droplets to prevent the precipitation or particle coalescence, which contributes to the stabilization of acidified milk drinks (Nobuhara et al., 2014) during the processing and storage.

Pectin is an anionic polysaccharide and contains more than 65% gal-acturonic acid (GalA) by weight as well as has both smooth regions (homogalacturonan) and branched hairy regions (rhamnolagacturonan) (May 2000; Voragen, Pilnik, Thibault, Axelon, & Renard, 1995). With at least 50% methyl esterification in GalA, HM-pectin is commonly used as stabilizers in acidified milks. Under acidic pH conditions, the presence of HM-pectin can significantly influence the stability of protein dispersions (Liu, Nakamura, & Corredig, 2006; Nakamura, Furuta, Kato, Maeda, & Nagamatsu, 2003) while the steric repulsion plays a major role in the caseins stabilization of acidified milks. Because of the negatively charged and the uncharged polysaccharide chains, HM-pectin can adsorb on caseins and form a self-supporting network which then stabilizes acidified milks (Tromp, De Kruif, van Eijk, & Rolin, 2004). Furthermore, the steric hindrance effects in combination with the secondary adsorption of HM-pectin partially contribute to the protein stabilization as well (Jensen, Rolin, & Ipsen, 2010). However, pectin is extracted from citrus or apple pomace, thanks to the resource shortage as well as the low extract rate, the cost of pectin has been

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rising in recent years. On the other hand, the feeling in the mouth of drinks stabilized by HM-pectin sticks thickly, which also restricts its application range.

SSPS is polysaccharide having a pectin-like structure. It is composed of a galacturonan backbone branched by β-1,4-galactantan, α-1,3- or α-1,5-arabinan chains, and homoga-lacturonan (Nakamura, Furuta, Maeda, Nagamatsu, & Yoshimoto, 2001; Nakamura, Furuta, Maeda, Takao, & Nagamatsu, 2002a,b). SSPS is also anionic polysaccharide and the steric repulsive forces dominate the interactions in dispersions, whereas negative charges originating from the GalA impose the electric repulsive forces on the droplets of the SSPS-caseins complex (Nobuhara et al., 2014). It has been demonstrated that the stabilizing properties of SSPS are comparable to pectin when SSPS used as a stabilizer in acidified drinks. In addition, under relatively high acidic pH conditions, the acidic drinks have lower viscosity values than those of beverages stabilized by pectin (Asai et al. 1994; Nakamura et al., 2003). Besides, SSPS could provide human health benefits by lowering blood cholesterol, improving laxation as well as reducing the risk of diabetes (Shorey, Willis, Lo, & Steinke, 1985; Tsai, Vinik, Lasichak, & Lo, 1987). Thus, SSPS has been recently commercialized and widely used as a stabilizer in acid milk dispersions, the addition of which has a higher ability than HM-pectin to enhance the stability of acidified milks at pH range of 3.0–4.0. When the pH ranges from 4.0 to 4.6, the ability of SSPS is lower than HM-pectin. Since SSPS is extracted from the soybean cotyledons with sufficient resource, the exploration of novel stabilizers based on SSPS with high ability to stabilize milk drinks under pH between 4.0 and 4.6 is needed.

In recent years, the interest in OSA modified starches increases rapidly while the chemical modification of starch with OSA has been already achieved by a standard esterification reaction (Bhosale & Singhal, 2006; Liu et al., 2008). However, no report was found about the technique of OSA modified SSPS so far. It could be indicated that compared to ordinary SSPS, the OSA modified SSPS molecules become amphiphilic by attaching hydrophobic groups to the repeat glucose units. The modification of polysaccharide chains to gain higher molecular weight SSPS (SSPS-HMW) is an efficient access to giving them new properties and functions (Nobuhara et al., 2014).

Objectives of this study were to modify SSPS by the esterification with OSA and investigate the factors that affect reaction between OSA and SSPS. Furthermore, after the novel modified SSPS was gained, characterization measurements and morphology analysis were taken to determine the milk protein stabilization properties of OSA-SSPS to stabilize the milk dispersions in acidic pH conditions.

2. Materials and methods

2.1. Materials

SSPS (crude protein 6.3%, crude fat 0.7%, soluble polysaccharides 76%, ash 7.4%, moisture 5.6%) was donated by Quanzhou Weibo Food Co. Ltd. (Fujian, China). HM-pectin (Lemon HM pectin) was obtained from CP Kelco Co. Ltd. (Lille Skensved, Denmark). Powdered skimmed milk (medium heated type) was obtained from Anchor Milk Co. Ltd. (New Zealand); 2-Octen-1-ylsuccinic anhydride (OSA) was purchased from Vertellus Health & Specialty Products LLC Co. Ltd. (Indianapolis IN, USA); Nile Blue was obtained from Sigma–Aldrich, Inc. (St. Louis, MO, USA). Tween-20 was obtained from Wako Chemical Co., Ltd. (Tokyo, Japan). All chemicals and reagents were of analytical grade. All solutions were prepared by using deionized water unless specified.

2.2. Preparation of OSA-SSPS

SSPS (10 wt%) was dispersed in water and stirred for 60 min in water bath at 40 °C. The sample typical total weight was 100 g. The pH value of the completely solubilized dispersion was adjusted to pH 8.5 and the proportion of OSA and SSPS was 1:7 (w/w), so for a 10 wt% aqueous solution of SSPS, an equal volume of 1.43 wt% OSA was added slowly with stirring and keeping the pH staying in 8.5 by the dropwise addition of NaOH (0.5 mol/L) for 35 min (Zhu, Li, Chen, & Li, 2013). After then, the mixture was adjusted to pH 5.0 by stepwise adding 0.1 mol/L HCl and then dialyzed against distilled water for 48 h at 4 °C. OSA-SSPS was finally obtained by freeze-drying to yield a OSA-SSPS free-flowing powder. To observe the effect of OSA concentration on the properties of SSPS modified products, the proportions of OSA and SSPS in mixture solutions ranging from 0:1 to 1:15 were used. Other steps were carried out as described above. To evaluate the effect of the heating temperature, the solutions were heated in water baths at 30, 35, 40, 45, 50 °C for 35 min. Other steps were carried out as described above. To study the effect of pH, the solutions were adjusted to pH 7.5, 8.0, 8.5, 9.0, 9.5. Other steps were carried out as described above. To investigate the effect of reaction time of OSA and SSPS, the mixture solutions were heated at 40 °C for 30 min, 35 min, 45 min, 50 min, 60 min, respectively. Other steps were carried out as described above.

2.3. Preparation of model acidified milks

The skimmed milk powder was dispersed in deionized water to reach a protein concentration of 2.0 wt%. OSA-SSPS, SSPS were dissolved in water respectively with concentration of 1.0 wt%. The well-dispersed skimmed milk dispersion and the polysaccharide solution were then mixed (Nobuhara et al., 2014). The pH value of the mixture was acidified to 3.6–4.6 by stepwise adding 0.1 mol/L mixed acids solution. The solution was then homogenized at room temperature with a homogenizer (T25, IKA Co. Ltd.) at 8000 rpm for 2 min. The final concentration of milk protein and OSA-SSPS or SSPS in model acidified milk was 1.0 wt% and 0.5 wt%, respectively.

2.4. Evaluation of acidified milk dispersion stability

2.4.1. Precipitate weight rate determination and measurement of turbidity of the upper layer

To separate destabilized protein particles as a precipitate in the bottom, model acidified milk (20 ml), separately prepared with OSA-SSPS, SSPS, was centrifuged at centrifugal acceleration 4000 g for 30 min in a centrifugation tube. After centrifugal treatment, the upper layer was decanted into another centrifugation tube to collect the precipitate and the upper layer, respectively. The precipitate was freeze-dried overnight, and then its weight was determined. The upper layer was diluted 20-fold with lactic acid solution, adjusted to a pH of 4.0, and then subjected to turbidimetric measurements at 550 nm by using a UV spectrophotometer (UV–2400PC, Shimadzu, Japan).

2.4.2. Dynamic light scattering (DLS) measurement

The size distributions of model acidified milk samples were monitored by a Zetasizer Nano-ZS instrument (Malvern Instruments, Worcestershire, U.K.) equipped with a 4 mW He-Ne laser (633 nm wavelength). The samples were placed in a 1 cm × 1 cm cuvette (PCS8501) and analyzed three times at 25 °C with a fix scattering angle of 173°. The apparent average hydrodynamic diameter (D_h) and polydispersity index (PDI) were obtained. The model acidified milk dispersions were 100-fold diluted to avoid the multiple scattering.