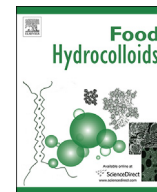


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The structure of soy soluble polysaccharide in aqueous solution

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ABSTRACT

Soybean soluble polysaccharide (SSPS) extracted from soybean cotyledons is an acidic polysaccharide containing a protein fraction. Small angle X-ray scattering (SAXS) and static light scattering (SLS) were used to reveal the structural conformation and nano-structural arrangement of SSPS in aqueous solutions aiming to gain more information on the functional properties of SSPS. Three samples, differentiated by their extraction processes, namely SSPS-L; -M; and -H, were used. NMR results show that SSPS has a similar structure regardless of the differences in the extraction conditions. The Mark–Houwink constants were determined to be 7.52×10^{-4} and 0.473 for K and α respectively indicating that SSPS is a flexible random coil in solution. SAXS profiles revealed power law functions ($I(q) \sim q^{-\alpha}$) with an exponent of -1 signifying the presence of rigid rods. Due to the overall large size of SSPS, it is thought that SAXS focused on single branches of SSPS. SAXS models confirmed that the nano-structural conformation of SSPS remains unaltered due to the presence of sodium nitrate salt, neither is the conformation affected by changes in pH nor concentration.

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1. Introduction

A by-product obtained during the production of tofu and soybean protein, named soybean soluble polysaccharide (SSPS), an acidic polysaccharide containing a protein fraction, has been suggested as an emulsifier for beverage emulsions (Maeda, 2000). SSPS is composed of a main rhamnogalacturonan (RG) backbone branched by β -1,4-galactan and α -1,3- or α -1,5-arabinan chains, and homogalacturonan (Nakamura, Furuta, Maeda, Nagamatsu, & Yoshimoto, 2001; Nakamura, Furuta, Maeda, Takao, & Nagamatsu, 2002). SSPS has been used as a functional food ingredient in many different industrial applications (Maeda, 2000). It has been suggested that SSPS could be used in flavor emulsions, because of its high water solubility, low bulk viscosity, high temperature stability, emulsifying properties and its ability to form strong interfacial films (Furuta & Maeda, 1999). This industry has however been dominated by a well known polysaccharide named gum Arabic (GA) from *Acacia Senegal*. GA is commonly used because of its high water solubility over a wide range of concentrations without being highly viscous and ability to create a strong protective film around the oil droplet. The combination of this behavior and of the structure and composition confers on the highly valued emulsifying,

stabilizing, thickening and suspending properties (Cozic, Picton, Garda, Marlhoux, & Le Cerf, 2009).

GA and SSPS stabilize emulsions using different mechanisms. GA prevents emulsion aggregation by causing steric and electrostatic repulsion between oil droplets. The hydrophobic polypeptide chains adsorb on the surface of oil droplet and act as anchor, while the hydrophilic polysaccharide portions prevent aggregation by surrounding the oil droplets in a thick charged layer (Nakamura, Yoshida, Maeda, Furuta, & Corredig, 2004b). On the other hand, Nakamura, Maeda, and Corredig (2006) reports that the protein fraction associated with SSPS anchors the carbohydrate moieties to the oil/water interface while the long hydrophilic chains create a thick hydrated layer of about 30 nm which prevents droplet coalescence by steric repulsions.

Attempts to replace GA by other polysaccharides such as SSPS, pectins and modified starches have been tried due to the cost and availability constraints associated with GA. However GA remains the most important because in some applications, GA has technical advantages which make it difficult to be substituted completely (Cozic et al., 2009). The precise chemical and molecular structure differs according to the botanical origin of the gum, and these differences are reflected in some of the analytical properties of the gum. As a result, the commercial value and functional uses of GA largely depends on the origin. To this end, the functional properties of SSPS are also thought to be dependent on the physical properties of SSPS including molecular mass and structural conformation.

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Analysis of structural components and molecular construction showed that SSPS has pectin-like sugar composition with a small difference in the amount of uronate present (Nakamura et al., 2001). Currently structural analysis using the ratio of static to dynamic light scattering parameters (radius of gyration [R_g] and hydrodynamic radius [R_h] respectively) revealed that SSPS has a highly branched globular shape (Wang, Huang, Nakamura, Burchard, & Hallet, 2005). Ikeda, Funami, and Zhang (2005) and Nakamura, Fujii, Tobe, Adachi, and Hirotsuka (2012) also reported SSPS to be a star like polymer with a number of branches from the main backbone. Polymer conformation has a direct bearing on the physical properties of the polymer. Some properties that can be influenced include solution viscosity, solution light scattering, and mechanical properties. In line with the previous work, the motive of this research was to investigate the internal nano-structure of SSPS using SAXS as the main experimental tool in order to find possibilities of new applications of this polysaccharide. This is the first time that SAXS technique has been performed on SSPS.

2. Experimental

2.1. Materials

Soyfibre-S or SSPS, type SSPS-L, -M and -H, was obtained from Fuji Oil Co. Ltd. (Tokyo, Japan).

2.2. Preparation of SSPS

SSPS-L and -M were prepared using the method of Nakamura, Takahashi, Yoshida, Maeda, and Corredig (2004a). SSPS-L and M were extracted from *okara* (soybean residue after extraction of oil and protein) using hot water by heating at 120 °C, pH 3.0 for 2 h and 120 °C, pH 4.0–5.0 for 2 h, respectively. Insoluble materials were then removed by centrifugation and the extract was desalted by electric dialysis before being spray dried. The sample named SSPS-H in this paper was prepared using the method of Nakamura et al., (2012). *Okara* was heated at 120 °C at pH 4.0 for 2 h. Insoluble residue was then centrifuged out, the extract desalted and then concentrated by a rotary evaporator to 20%w/w before being freeze-dried.

2.3. Intrinsic viscosity determination

Ubbelohde viscometer (Viscometer No.W-92, Kusano Kagaku Kikai Suisakusho, Japan) was used to measure the specific viscosities of SSPS samples at 25 °C with concentrations ranging from 0.42 to 4.0%w/v in 0.1 M NaNO₃. The Mark–Houwink values of K and α were determined from a double-logarithmic plot of the intrinsic viscosity, $[\eta]$, against weight-average molecular weight, M_w , of SSPS samples for which the M_w had been determined by SLS measured as described in Section 2.4 below.

2.4. Molecular weight determination

Three types of SSPS described above were used. An Optilab rEX (Wyatt Technology Corporation, USA) was used to determine the change in SSPS solution refractive index (RI) with the change in solute concentration, known as the dn/dc (mL/g) value. Calibration was done using anhydrous sodium chloride dissolved in water at 690 nm and 25 °C. A multi-angle laser light scattering photometer, DAWN EOS (Wyatt Technology Corporation, USA) was used to determine weight-average molecular weight (M_w) and radius of gyration (R_g). Instrument was calibrated by toluene filtered through a 0.2 μ m filter. Measurements of SSPS were carried out at 690 nm using dn/dc values of 0.065, 0.165 and 0.735 mL/g as determined by

Optilab rEX (Wyatt Technology Corporation, USA) for SSPS-L; M; and H dissolved in 50 mM NaCl respectively. The SSPS solutions were filtered (0.2 μ m) and injected into the instrument cell for batch measurement and the data was analyzed by Zimm plot method. Data were presented as means of duplicates.

2.5. Nuclear magnetic resonance

Dried samples of SSPS (0.5%) were dissolved by magnetic stirring in deuterium oxide (99.9%; EURISCO-TOP, France) at approximately 25 °C over night to ensure complete dissolution. Trimethylsilane (TMS) (0.06%) was added in the solutions as a standard for NMR spectroscopy. Data was gathered from the NMR machine (ALPHA 600; JEOL, Japan) after 8 scans using automatic shimming at field strength of 14.096 T and a spin of 15 Hz and a sample temperature of 60 °C. Data was analyzed using the Delta Software.

2.6. Nano-structure determination using SAXS

The SAXS measurements were carried out using Nano Viewer (Rigaku Co., Japan) at an applied voltage and filament current of 40 kV and 30 mA respectively. Incident X-ray was generated by high intensity micro-focus rotating anode X-ray generator (MicroMax-007HF) and monochromatized to 0.154 nm. The scattered X-ray was detected with a Dectris 100k, Pilatus (Rigaku Co., Japan) positioned approximately 800 mm from the sample. Samples (SSPS solutions which were completely dissolved and hydrated in distilled water and/or NaNO₃ by magnetic stirring) were injected into a metal U-plate sample holder covered with a kapton plastic foil on both sides. Scattering intensities were accumulated for 1 h for all the samples. All measurements were carried out at approximately 25 °C. The excess scattering intensities were calculated by subtracting the scattering intensities of solvent from those of the SSPS solution. The data are presented as intensity, $I(q)$ (at absolute units) as a function of the scattering vector given by $q = (4\pi \sin \theta / 2) / \lambda$, where θ is the scattering angle and λ (nm) is the wavelength (Kratky and Glatter, 1982).

3. Results and discussions

3.1. Intrinsic viscosity $[\eta]$ and average molecular weight (M_w)

3.1.1. Intrinsic viscosity

Huggins and Kraemer plots from the calculated values of η_{sp}/C (η_{sp} = specific viscosity) and $\ln(\eta_{rel})/C$ (η_{rel} = relative viscosity) plotted against the concentrations (C) of SSPS-L, M and H were relatively linear and converged to a common intercept at $C = 0$. Thus the $[\eta]$ of SSPS-L, M, and H in 0.1 M NaNO₃ were found to be 0.18, 0.27 and 0.425 dL/g respectively. The obtained intrinsic viscosity values, especially for SSPS-L and -M, differ from the literature values of 0.495 and 0.65 dL/g reported by Furuta and Maeda (1999) and Wang et al., (2005) respectively. This may be attributed to the differences in the pH, temperature, and time combinations during the extraction of the polysaccharides as seen from the samples used by Furuta and Maeda (1999) and Wang et al. (2005).

When the intrinsic viscosity of SSPS dissolved in variable sodium nitrate concentrations was measured, there was no significant change observed for SSPS-L and -M as shown in Fig. 1. SSPS-H had a high intrinsic viscosity value when dissolved in water which decreased to a constant value of approximately 0.43 dL/g when dissolved in increasing concentrations of sodium nitrate. Intrinsic viscosity is a measure of the hydrodynamic volume occupied by the individual polymer molecules in isolation (Richardson & Kasapis, 1998). The solution properties of macromolecular polysaccharides

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