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Rheological properties of natural low-methoxyl pectin extracted from sunflower head

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ABSTRACT

Rheological properties of natural low-methoxyl sunflower pectin have been investigated. Sugar composition and molecular parameters of SFHP were characterized. The M_w and M_n of SFHP is 605.6 kDa, 111.0 kDa, respectively, thereby giving a moderate polydispersion index of 5.50. Huggins plot indicated a stiff rod-like conformation of SFHP in dilute solution. Dilute SFHP solution (<1.0%, w/w) had low viscosity due to lack of interactions. Increasing of pectin concentration resulted in rapid increase of solution viscosity since SFHP has large hydrodynamic size. The aggregation of pectin became obvious by lowering pH to below 3.0. In pH range from 4.0 to 7.0, there is no difference in rheological behaviors of 1.0% SFHP solution. When heated, viscosity of SFHP solutions gradually decreased and attained equilibrium state at over 60 °C. In the case of 3.0% (w/w) SFHP solution, the network structure has been formed and the solution presented good resistance to environmental change.

1. Introduction

Pectin is a structural heteropolysaccharide contained in the primary cell walls of terrestrial plants. The main structural features of pectin comprise homogalacturonan (HG), rhamnogalacturonan I (RGI) and rhamnogalacturonan II (RGII). HG is the linear polymer consisting of 1,4-linked α-D-galacturonic acid (GalA) backbone. RGI consists of the repeating disaccharide [-4)-α-D-GalA-(1-2)-α-L-Rha-(1-], whereas RGII has a backbone of HG with complex side chains attached to the GalA residues (Mohnen, 2008; Ridley, O'Neill, & Mohnen, 2001; Willats, McCartney, Mackie, & Knox, 2001). Pectin contains from a few hundred to about 1000 saccharide units corresponding to average molecular weights (MW) from 50,000 to 150,000 Da (Sriamornsak, 2003). Traditionally, pectins are categorized as high methoxyl pectin (HMP) and low methoxyl pectin (LMP) with degree of methoxylation (DM) of >50% and <50%, respectively.

Both MW and molecular structure have a profound impact on rheological behaviors and gelling properties of pectin (Fraeye, Colle, et al., 2010; Willats, Knox, & Mikkelsen, 2006). LMP usually form gels in the presence of Ca^{2+} ions and over a wider range of pH values, with or without sugar. Amidated LMPs need less Ca^{2+} for gelling and the hydrogen bonds between amide groups can promote the gel formation of amidated LMPs at low pH (≤3.5) (Löfgren, Guillotin, & Hermansson, 2006; Racape & Thibault, 1989). Some pectins are naturally acetylated and acetyl groups drastically decrease the binding strength of pectin with Ca^{2+} ions (Ralet, Crepeau, Buchholt, & Thibault, 2003).

Rheological behaviors of pectin in solution also highly depend on environmental conditions such as pH, concentration, temperature, sugars and salts (Evageliou, Richardson, & Morris, 2000; Lootens et al., 2003; Löfgren, Guillotin, Evenbratt, Schols, & Hermansson, 2005). In dilute solution, pectin molecules are apart from each other. Pectin conformation is mainly affected by pectin-solute and pectin-solvent interactions and solution viscosity is sensitive to variation of environmental conditions (Fraeye,

Abbreviations: DAc, degree of acetylation; DAm, degree of amidation; DM, degree of methylesterification; GalA, galacturonic acid; HG, homogalacturonan; HMP, high methoxyl pectin; HPAEC-PAD, High Performance Anion Exchange Chromatography-pulsed Amperometric Detector; HPSEC-MALLS, High Performance Size Exclusion Chromatography Multiangle Laser Light Scattering; MW, molecular weight; M_w, weight-average molecular weight; M_n, number-average Molecular Weight; LMP, low methoxyl pectin; RGI, rhamnogalacturonan I; RGII, rhamnogalacturonan II; Rha, rhamnose; SFHP, sunflower head pectin.

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Duvetter, Doungla, Van Loey, & Hendrickx, 2010). With concentration increasing, pectin molecules can aggregate to construct three-dimensional network structure leading to the formation of thick solution or gel. Particularly, stable junction zones consisted of cooperatively ordered chains linked together throughout non-bonded interactions such as hydrogen bonding can bring good resistance to environmental change (Braccini, Rodríguez-Carvajal, & Pérez, 2005).

LMP has attracted a great deal attention in recent years due to its applications in functional foods or pharmaceuticals (De'Nobili, Pérez, Navarro Stortz, & Rojas, 2013; May, 1990; Urestia, López-Ariasa, González-Cabrialesa, Ramíreza, & Vázquez, 2003). Artificial LMPs with designed DM have been manufactured from commercial HMP by enzymatic or chemical deesterification (El-Nawawi & Heikal, 1995; Ralet, Dronnet, Buchholt, & Thibaul, 2001), whereas the high cost is the major problem in applications. As the alternative, natural LMPs are safe and cheap. Nevertheless, LMPs from different sources have various physicochemical properties due to the different structural features.

Sunflower pectin is a natural LMP typically with MW of 30,000–500,000 g/mol, GalA content of 70–90%, DM of 10–40% and acetylation content of 2–4% (w/w) different from varieties (Iglesias & Lozano, 2004; Miyamoto & Chang, 1992; Sahari, Akbarian, & Hamedi, 2003). The chelators-assisted acidic isolation of sunflower pectin has been fully studied in 1970s–1990s (Chang, Dhurandhar, You, & Miyamoto, 1994; Kim, Sosulski, & Campbell, 1978; Kim, Sosulski, & Lee, 1978). However, the rheological properties of SFHP have not been deeply investigated.

In this study, the rheological properties of LMP extracted from the sunflower grown in north part of Xinjiang province (China) were investigated. Sugar composition and molecular parameters of SFHP were characterized in order to understand its structural features. Huggins plot of SFHP was plotted for analyzing the conformational transitions of SFHP in dilute solution. The rheological behaviors of SFHP solution employing different SFHP concentration, pH and temperature were investigated.

2. Materials and methods

2.1. Materials

Oilseed sunflower head was harvested in Xinjiang, China. The sun-dried sunflower heads were finely ground before use with an analytic mill (A11 Basic; IKA, Staufen, German). All the analytical-grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China) and used without further purification.

2.2. Extraction of sunflower head pectin

Ground sunflower head of 50 g was washed with 1500 mL deionized water for 30 min at ambient temperature for removal of water-soluble impurities. Then, the pectin was extracted by addition of 1500 mL 0.5% (w/v) ammonium oxalate at 85 °C for 45 min. After filtration, the filtrate was mixed with two volumes of 4 °C acidified ethanol (0.2% HCl, v/v) and incubated for 1 h for fully development of pectin lump. The obtained pectin was subsequently washed with acidified ethanol (0.04% HCl v/v) and 70% (v/v) ethanol for complete removal of Cl^- (detected by $AgNO_3$). Finally, the pectin was dried at 40 °C for 20 h and stored at 4 °C before analysis.

2.3. Determinant of DM, DAm and DAc

Degree of methylesterification (DM), degree of amidation (DAm) and degree of acetylation (DAc) of SFHP were determined by titration method according to National Standard of China GB25533-2010 "Food Additive Pectin".

SFHP solution (0.5000 g/100 mL deionized water) was titrated by 0.1 mol/L NaOH using phenolphthalein as the indicator and the volume consumed was V_1. Afterward, saponification of pectin was initiated by addition of 20.0 mL 0.5 mol/L NaOH and was stopped by addition of 20.0 mL 0.5 mol/L HCl. The excessive HCl was titrated by 0.1 mol/L NaOH and the volume consumed was V_2. After that, the solution was mixed with 20 mL 2.5 mol/L NaOH in a 500 mL flask connecting to a condenser, whose delivery line was submerged into the mixture of 150 mL water and 20 mL 0.1 mol/L HCl. The mixture was distilled until 80~120 mL distillate was collected. The excessive HCl was then titrated by 0.1 mol/L NaOH using methyl red as the indicator and the consumed volume was S. Blank test was performed using 20.0 mL 0.1 mol/L HCl and the consumed volume of HCl was B. The value of $(B - S)$ was written as V_3.

For determining the amount of acetyl, 0.5000 g dried SFHP was dissolved in 25 mL 0.125 mol/L NaOH. After stirring for 1 h, the solution was diluted in a 50 mL volumetric flask to volume. A mixture of 20 mL diluted solution and 20 mL Clark's solution (contains 100 g $MgSO_4 \cdot 7H_2O$, 0.8 mL H_2SO_4 and 180 mL H_2O) was distilled until 150 mL distillate was collected. The distillate was subsequently titrated by 0.05 mol/L NaOH to pH 8.5 and the consumed volume was A. Deionized water was used as blank for titration and the consumed volume was A_0. The value of $(A - A_0)$ was assumed as V_4.

$$\mathrm{DM}\% = \frac{V_2(\mathrm{mL})}{V_1(\mathrm{mL}) + V_2(\mathrm{mL}) + V_3(\mathrm{mL}) - V_4(\mathrm{mL})} \times 100 \quad (1)$$

$$\mathrm{DAm}\% = \frac{V_3(\mathrm{mL})}{V_1(\mathrm{mL}) + V_2(\mathrm{mL}) + V_3(\mathrm{mL}) - V_4(\mathrm{mL})} \times 100 \quad (2)$$

$$\mathrm{DAc}\,(\%) = \frac{V_4 \times 10^{-3}(\mathrm{L}) \times 0.05\left(\frac{\mathrm{mol}}{\mathrm{L}}\right)}{0.5000(\mathrm{g}) \times 0.821} \times 194.14(\mathrm{g/mol}) \times 100 \quad (3)$$

2.4. HPSEC-MALLS

The molecular parameters of SFHP samples were determined using HPSEC-MALLS. The system mainly consists of a multi-angle light scattering photometer (DAWN-HELEOS; Wyatt Technology, CA, USA) equipped with a He–Ne laser at the wavelength of 658 nm, a differential refractometer (OptiLabrEX; Wyatt Technology, CA, USA). 100 μL of 0.15% (w/w) SFHP solution was passed through a column SB-806HQ (8.0 mm × 300 mm) (ShodexOHpak, Japan, exclusion limits 2×10^7 g/mol, pore size maximum 15,000) at a flow rate of 0.5 mL/min with 50 mM $NaNO_3$ as the eluent. The eluent was passed through a degasser (ERC-3215; ERC Inc., CE, Japan) before being pumped into the system using a binary HPCL pump (1525; Waters, MA, USA). All samples were filtered through a 0.45 μm nylon filter prior to injection to the system. A dn/dc value of 0.146 mL/g for LMP reported previously (Cameron, Luzio, Goodner, & Williams, 2008; Fishman et al., 1997) was taken for the determination of MW.

2.5. HPAEC-PAD

In a typical sample pretreatment procedure, a glass tube containing 5.0 mg SFHP and 0.5 mL deionized water was heated in boiling water for completely dissolution of SFHP. After addition of 4.0 mL 4 M trifluoroacetic acid (TFA), the tube was tightly sealed with stopper and subsequently incubated at 121 °C for 2 h in an