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The role of entanglement concentration on the hydrodynamic properties of potato and sweet potato starches

Li Guo [a,*,1], Jian Hu [b,2], Juanjuan Zhang [b,2], Xianfeng Du [b,2]

[a] School of Food Sciences and Engineering, Qilu University of Technology, Jinan, China
[b] Department of Food Sciences, Anhui Agricultural University, Hefei, China

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ABSTRACT

The hydrodynamic properties of potato starch and sweet potato starch in dilute and semi-dilute aqueous solutions were studied using a Ubbelohde viscometer, a transmission electron microscope, and steady shear rheological measurements. The results indicated that the potato starch solutions showed a linear shape of the η_{red} versus c curves. The sweet potato starch solutions presented a non-linear shape with a downturn in dilute solutions, or the concentrations were lower than entanglement concentration (c_e). The c_e values of the potato and sweet potato starch solutions were 0.43% and 0.54%, respectively. These findings indicated that the impact of the c_e value on the network formation of the potato starch solutions was much more significant compared with the impact on the sweet potato starch solutions. The potato and sweet potato starch solutions showed shear thinning behaviour hardly occurs when the concentrations were less than c_e, while shear thinning behaviour approached when the concentrations were equal to or greater than c_e. Similarly, the potato and sweet potato starch solutions rarely resembled a pseudoplastic state when the concentrations were lower than or equal to c_e, while the pseudoplastic behaviour developed when the concentrations were higher than c_e.

1. Introduction

Potato and sweet potato starches have been widely used in vermicelli, starch noodles, bakery foods, snack foods and confectionery products, etc., due to the similarly unique properties such as low gelatinization temperature, high water binding capacity, high paste consistency, and good paste clarity [1,2]. Among these properties, pasting behaviour is very important and is usually investigated by observing the change in viscosity of starches. The starch pasting behaviour in aqueous solutions depends on the size distribution of a starch granule and the ratio of amylose to amylopectin, etc. [3]. The starch granules in solutions are increasingly susceptible to shear disintegration as they swell, and soluble materials are released. A hot starch paste is a mixture of swollen granules and granule fragments, together with colloidally and molecularly dispersed starch granules. This depends upon the botanical source of the starch, water content and shearing during heating [4]. Starch hydrodynamic properties in aqueous solutions are a valuable tool to gain insight into the rheological properties of starch paste, which is of considerable technological importance in foods, pharmaceuticals, adhesives, etc. [5]. To determine the suitability of potato and sweet potato starch pastes for specific requirements, it is essential to understand the dynamics of starch in an aqueous solution. To date, many studies have focused on the effects that high concentrations have on the physicochemical properties of potato and sweet potato starches, but what their hydrodynamic properties are in low concentrations remains unclear, especially in dilute and semi-dilute aqueous solutions.

Polymer chains in the form of solvated random coils cannot overlap in a dilute solution. When increasing the concentration in the dilute region, the random coils begin to come into contact with one another, reaching the critical concentration (c^*) and then overlapping at the entanglement concentration (c_e) [6]. So, the c_e is defined as the boundary between the semi-dilute regime and the concentrated regime of a polymer solution. In the semi-dilute regime, polymer chains overlap with each other but do not entangle, whereas in the concentrated regime, polymer chains significantly overlap each other such that individual chain motion is constrained [7]. Thus, c_e marks the onset of significant coil overlap and interpenetration. What changes will occur in the viscometric

* Corresponding author.
E-mail addresses: guolizhuyuer@163.com (L. Guo), 309948964@qq.com (J. Hu), 1327198922@qq.com (J. Zhang), dxf@ahau.edu.cn (X. Du).
[1] Postal address: No. 3501, Daxue Rd., Changqing District, Qilu University of Technology, Jinan, Shandong Province 250353, China.
[2] Postal address: No. 130, Western Changjiang Road, Anhui Agricultural University, Hefei City, Anhui Province 230036, China.

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behaviour of the starch solutions when the concentrations are more or less than c_e? In general, c_e is influenced by factors such as relative molecular weight, solvent properties, amylopectin branch chain length, etc [6]. In this paper, water was used as the solvent. Starch granule size distribution and amylopectin branch chain length were first analysed using a laser light scattering particle size analyzer and a high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD), respectively. Secondly, the entanglement concentration (c_e) was determined to study the chain dimensions of the potato and sweet potato starches in dilute solutions by utilising a Ubbelohde viscometer. Thirdly, the changes of the network formation were observed during the gelatinization and retrogradation of starch solutions by using a transmission electron microscope (TEM). Finally, the hydrodynamic properties of starch in dilute and semi-dilute aqueous solutions were analysed using steady shear rheological measurements. These insights may help to accurately regulate the concentrations of potato and sweet potato starch solutions to obtain the desired processing properties such as texture, taste, viscosity, consistency, etc.

2. Materials and methods

2.1. Materials

Potato starch (Pcode: 10360201) was ordered from Sigma-Aldrich. Sweet potato starch came from Jincheng Co. (Shandong, China). Isoamylase (3,000,000 U/mg) from *pseudomonas amylodermosa* was obtained from Sigma-Aldrich, and the activity was defined by the manufacturer. The starches were defatted and deproteinized using methanol (85%, v/v) and chloroform/n-Butyl alcohol (4:1, v/v) as solvents, respectively. Total starch content was measured [8]. The amylose content was determined using an iodine colorimetric method [9]. The contents of moisture, protein, lipid, phosphorus and ash of starch were analysed according to the protocols of the Association of Official Analytical Chemists [10].

2.2. Starch structure characteristics

2.2.1. Starch granule size distribution

Particle size analysis was carried out using a laser light scattering particle size analyzer (Malvern Mastersizer Hydro 2000 MU, Malvern Instruments Ltd., UK). Starch granules were suspended in distilled water and then stirred at 2000 rpm. A general analysis model was used with particle refractive and absorption indices of 1.53 and 0.01, respectively. The refractive index of water as the dispersant was 1.33. Detection of the starch particles occurred within the range (0.02-2000 μm). The obscuration in all the measurements ranged from 9% to 13%. Particle sizes were defined in terms of the volume weighted mean [$D(4, 3)$], 10th percentile [$d(0.1)$], 50th or median [$d(0.5)$], 90th percentile [$d(0.9)$] and surface weighted mean [$D(3, 2)$] using to determine the specific surface area (m^2/g). Assays were done in triplicate, and results are expressed as means ±standard deviation of triplicate.

2.2.2. Amylopectin and amylose isolation

Granular starch (2.5 g) was dissolved in 50 mL of 90% dimethyl sulfoxide (DMSO) by heating in a boiling water bath with constant stirring for 1 h to make sure no gelatinous lumps remained. After dissolution of starch, the solution was placed at room temperature for 10 min and then absolute ethanol (200 mL) was slowly added with continuous stirring for 15 min to precipitate the dissolved starch. The slurry was centrifuged at 3000 rpm for 10 min. The supernatant was discarded and the sediment resuspended in absolute ethanol (50 mL) and then centrifuged at 3000 rpm for 10 min. The precipitate was dispersed in 50 mL of 90% DMSO in a Erlenmeyer flask sealed with aluminum foil, and then heated in a boiling water bath with constant stirring for 1 h, and subsequently cooled at room temperature for 15 min. A solution of 6% 1-Butanol and 6% isoamylalcohol in deionized water (400 mL) was added to the flask. The mixture was stirred and placed in a 95 °C water bath for 1 h, and the mixture was then cooled to room temperature for about 20 h. The mixture was then centrifuged (8000 rpm, 10 min). The supernatant containing amylopectin was concentrated under vacuum to ~100 mL at 60 °C using a rotary evaporator (Hei-VAP Advantage ML/HB/G3, Heidolph, Germany). Two volumes of absolute ethanol were added to the concentrated fraction to obtain amylopectin. The precipitate containing amylose was washed with ethanol (20 mL) followed by acetone (20 mL), and freeze-dried for 24 h. The average degree of polymerization ($\overline{DP}$) of amylose was calculated from dividing total carbohydrates by the reducing residues. Total carbohydrates were determined by the phenol-sulfuric acid method [11] and reducing residues were analysed by the method of Somogyi [12].

2.2.3. Distributions of amylopectin branch chain length

Amylopectin (0.1 g, dry basis) was dispersed in 2.5 mL of 90% DMSO and heated in a boiling water bath for 15 min with magnetic stirring (350 rpm), and then 2.5 mL of 50 mM sodium acetate buffer (pH 5.5) was added and the solution was cooled to 37 °C. Subsequently, 10 μL of isoamylase was added to the solution and incubated at 37 °C for 12 h with slow stirring (200 rpm). The enzyme was inactivated by boiling for 10 min. Double distilled water was added to dilute the sample to a concentration of 1.0 mg/mL. An aliquot (50 μL) was filtered through a membrane filter (0.45 μm) and then analysed by HPAEC. The distribution of amylopectin branch chain length was analysed by HPAEC-PAD on a Dionex ICS 3000 instrument (Sunnyvale, CA, USA). The analytical column was CarboPac PA-100 anion-exchange column (4 × 250 mm), combined with a CarboPac PA-100 guard column (4 × 50 mm). The flow rate was 0.5 mL/min and the injection volume was 25 μL with a carbohydrate concentration of 1 mg/mL. The samples were eluted at 0.5 mL/min with a gradient of NaOAc made by mixing eluent B (1 M NaOAc) into eluent A (0.25 M NaOH) as follows: 0–15 min from 15 to 34%; 15–26 min from 34 to 40%; 26–52 min from 40 to 49%; 52–54 min from 49 to 100%; and finally return to start mixture at 58–60 min from 100 to 15%. PAD signal was converted to carbohydrate content.

2.3. Starch viscosity characteristics

Capillary viscometry was performed using a Ubbelohde viscometer and immersed in a thermostated bath at 65 ± 0.1 °C to prevent starch retrogradation from occurring. Aqueous solutions of potato and sweet potato starch concentrations (0.01–1.0 g/dL) were prepared and then heated at 90 °C for 30 min to completely gelatinize the starch granules prior to viscosity measurements. Relative viscosity (η_r) and specific viscosity (η_{sp}) were calculated by the following equations [13]:

$$\eta_r = \frac{t}{t_0} \quad (1)$$

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

where t and t_0 are the flow times of polymer solution and the pure solvent, respectively. The c_e values were determined by using the plots of η_{sp} versus concentrations (c).

2.4. TEM

On the basis of the c_e values, the potato and sweet potato starches were dispersed in deionized water to prepare the starch dispersions with different concentrations around c_e (0.1–1.0%,