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Rheological and Thermal Properties of Potato Starch

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Abstract: Particle size, rheological and thermal properties of potato starch from Yunnan province of China was investigated. The particle size ranges from 0.429-102.3 μm determined by laser light-scatter. The major flow type of 6 w/v% potato starch was shear-thinning fluid even the shear rate up to 800·s^{-1}, and the gel formed by 6 w/v% potato starch fell to weak gel for its little difference between G′ and G′′, high dependence on frequency and low value of G(Pa). The hardness and cohesiveness of potato starch gel were 31.3 g and 131.9 g·s, respectively. The thermal properties of potato starch were also determined by DSC at the starch:water=3:1. The T_o, T_p, and $\triangle H$ of potato starch were 62.23℃, 67.31℃, and 2.22 J·g^{-1}.

Key Words: potato starch; gelation; rheological behavior; DSC

China is one of the leading producers of potato in the world. Starch is the main component of potato tuber, making up 3/4 of its dry matter. The size of starch granules present in potato tuber cells ranges from 5-100 μm. Potato starch play an important part as a food product and raw material in industry[1].

Starch is composed of two fractions of different chemical composition, structure and properties. In fact, they should be considered as separate chemical compounds. One of them is amylose which occurs as a linear chain of glucose residues connected by α -1,4 glycosidic linkages. The molecules of amylose in aqueous solvents can have three different forms, i.e. helix, interrupted helix and random coil. In the helix, each coil contains 5-7 glucose residues. In the interrupted helix, the molecule is supposed to be composed of long helical sections, each containing approximately 120 glucose residues with short regions of random coil between. In both forms, the coils are stabilized by intramolecular hydrogen bonds. The third amylose form is that of random coil(no helix). Apart from the linear amylose chains, there are also amylose molecules with long-chain branching involving α-1,6 glycosidic linkages. Amylose chains of potato starch are long and may be made up of up to several thousand glucose residues. The degree of polymerization (DP) of the linear chain is c. 2000 and that of a branched fraction c. 6000.

The other starch fraction is amylopectin, which is a ramified structure containing short chains of α-1,4 linkages connecting the glucose residues and α-1,6 linkages connecting the chains. The amylopectin molecules consist of A- and B-chains. The A-chains are shorter and, on average, they contain 15 glucose units. The B-chains are longer and have DP of 45. These chains are connected by α-1,6 glycosidic linkages making up ‘ clusters’ of several chains. The B-chains connect two or more cluster, each of them containing two to four closely associated A-chains. The ratio of A:B chain ranges from 4:1 to 9:1. The average chain length depends on the lengths of

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A– and B– chains and molar ratios. The average chain length for potato starch amylopectin consists of 22–23 glucose residues. Amylopectin contains 94%–96% α–1,4 glycosidic linkages and 4%–6% α–1,6 linkages. The associated clusters of A–chains are primarily responsible for the crystalline regions within the granule. The amorphous regions occur at 6–7 nm intervals, contain the majority of α–1,6 linkages and are relatively susceptible to hydrolytic agents. Overall, the amylopectin molecule is 10–15 nm in diameter and 120–140 nm long[1].

The properties of potato starch depend on many factors: genetic, climatic, soil, meteorological and also technological. Less wok has been done for the physical properties of potato starch from China. The aim of the present study is to characterize the rheological and thermal properties of potato starch produced in China.

1 Material and Methods

1.1 Materials

Potato starch obtained from Rungkai Co. Ltd., Yunnan province was used. 2–propanol was from Fisher Scientific (Fair Lawn, NJ).

1.2 Methods

1.2.1 Particle Size Analysis

The laser light–scatter (Mastersizer, Malvern Instruments Ltd., Malvern, UK) is based on the principle of laser ensemble light scattering. It falls into the category of non–imaging optical systems due to the fact that sizing is accomplished without forming an image of the particle onto a detector.

The Mastersizer employs two forms of optical configuration to provide its unique specification. The first is the well known optical method, called "conventional Fourier optics". The second is called "reverse Fourier optics", used in order to allow the measurement size range to be extended down to 0.05 μm. There are restrictions placed upon the sample presentation requirements in this configuration which limit its availability to particles dispersed in liquid suspension.

About 1 w/v% of starch suspension was obtained in screw cap glass tube with isopropyl alcohol. Tubes were vortexed (Scientific Industries, Inc., Bohemia, NJ) for about 5 min, the starch suspension was transferred into the instrument´s dispersion tank containing isopropyl alcohol to get the obscuration value about 15%–20%. Starch granule size was measured.

Figure 1 shows plots of volume percent of particles suspended in isopropyl alcohol over a range of particle diameter as determined by laser light–scattering analysis. The particle–size distribution was expressed as a percentage of the total volume, assuming spherical particles. In the potato starch industry, it is well known that large granules are more readily washed from the pulp and centrifuged during starch separation from juice water and they are less susceptible to pulverization after drying than small granules. Large granules are more susceptible to dextrinization and they yield better quality dextrins than small granules[1].

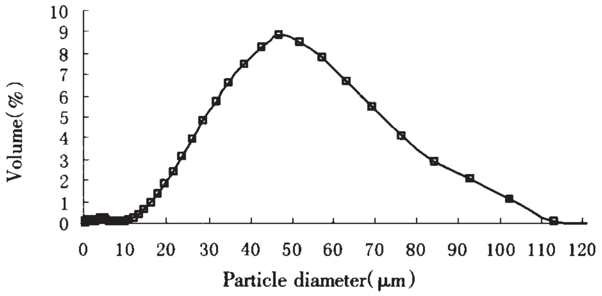

Fig. 1 Particle size distribution of potato starch dispersion

1.2.2 Rheological Measurements

Dynamic viscoelastic measurements were carried out using a Dynamic Stress Rheometer SR–500 (Rheometric Scientific Inc., Piscataway, NJ) with a cone plate geometry (25 mm in diameter, cone angle 0.0385 radians, 0.5 mm gap) and a strain of 5% (limit of linear viscoelastic strain was about 8%). Potato starch (6 w/v%) was dispersed in distilled water at room temperature and was heated to 95°C and then maintained at 95℃ for 30 min. The dispersion of 1 mL was poured directly onto the plate of the instrument, which was equilibrated to 25℃. For all the samples, measurements were made at a frequency of

1.0 Hz with amplitude of 1mrad over 12 h periods. A solvent trap was used to eliminate the evaporation of water. At the end of each run a frequency sweep was performed in the range between 0.1 and 10.0 Hz. All measurements were undertaken twice and agreed within ± 2%. Results reported are an average of the two measurements.

1.2.3 Gel Strength

Sample preparation was similar to above. Hot samples were transferred into storage jars and cooled to 22℃ and stored at that temperature for 24 h before the measurement of the gel strength. Measurement was performed using a texture analyzer (TA. XT2 Texture Analyser, Scarsdale, New York). A cylindrical flat-ended probe (11 mm) was used to compress the gel at a speed of 1.0 mm·s^{-1} for distance of 6 mm. Hardness and adhesiveness were computed from the instrument software. Triplicate measurements were performed and agreed within 2%.

1.2.4 Thermal Property

DSC measurements were performed on a Perkin Elmer DSC-7. Sample pans of aluminum from TA Instruments were used with an empty sample container as reference to balance the heat capacity of the sample pan. Potato starch (10-20 mg) was transferred into weighed sample containers, and the appropriate amount of water was added using a microsyringe to give a precalculated water: starch ratio (1:3). The final weighed samples (≤ 30 mg) were immediately hermetically sealed using a volatile sample sealer accessory and reweighed. The samples were allowed to equilibrate for about 1 h before DSC analysis to attain an even distribution of water. In the starch gelatinization studies, the sample was examined by DSC after the equilibration period. The samples were heated at 5℃·min^{-1} over a temperature range of 25-110℃. Indium (Melting points 156.6℃, enthalpies, $\triangle H$ 28.45 J·g^{-1}) was used as reference standards. The gelatinization temperature and enthalpy change were determined. Enthalpy change ($\triangle H$), onset temperature (T_o), peak temperature (T_p)and conclusion temperature (T_m) were recorded [2]. The data were calculated from duplicate.

2 Results and Discussion

2.1 Flow Behavior

The major types of fluid flow behavior can be described by means of basic shear diagrams of shear rate versus shear stress. With shear-shinning fluids, the curve begins at the origin of the shear stress-shear rate plot but is concave upward; that is, an increasing shear-thinning fluid is popularly called pseudoplastic. Shear-thinning may be thought of being due to breakdown of structural units in a food due to the hydrodynamic forces generated during shear[3]. Dispersion of potato starch exhibited shear-thinning up to shear rates of 1500·s^{-1} as shown by the shear stress vs shear rate curve(Fig. 2).

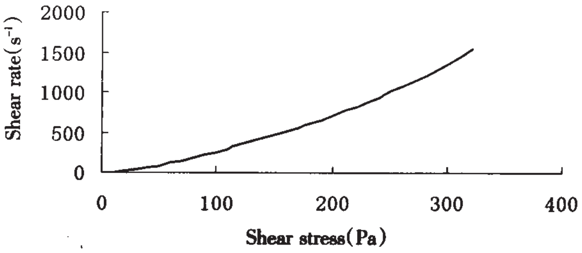

Fig. 2 Basic shear diagram of shear rate versus shear stress for 6% potato starch dispersion

Since the potato starch dispersion exhibited shear-thinning behavior up to shear rate of 300·s^{-1}, the power law model was used to describe that segment of shear-rate vs shear stress data of the dispersion from double logarithimic plot.

2.2 Mechanical Spectrum

Frequency sweep studies in which G′ and G″ are determined as a function of frequency(ω) at a fixed temperature. Based on frequency sweep data, one can designate "true gels" when the molecular rearrangements within the network are much reduced over the time scales analyzed, such that G′´ is higher than G″ throughout the frequency range and is almost independent of frequency (ω). In contrast, for "weak gels", there is higher dependence on frequency for the dynamic moduli, suggesting the existence of relaxation processes occurring even at short time scales, and lower difference between moduli values. Additionally, with a dilute biopolymer solution, G″ is larger than G′ over the entire frequency range, but at high frequency, G′ is proportional to ω^2 and G″ is proportional to ω. For a concentrated biopolymer solution, G″ is larger than G′ at lower frequencies, but the G′ and G″ curves intersect at a crossover frequency; at frequencies higher than the crossover frequency, values of G′ are higher than those of G″ [3].

The mechanical spectra, G′ and G″ versus frequency at certain temperature are compared in Figure 3. It is readily seen that G′ has remained higher than G″ for almost all frequency. This indicates that the sample is indeed in a gel state. But the gel strength, as monitored by G′ in Figure 4, is low. And G′ shows higher frequency dependence, an attribute of a weak gel.

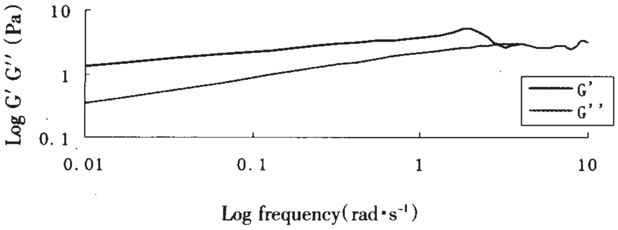

Fig. 3 Storage (G´) and loss (G´´) moduli versus frequency (Hz) of 6% potato starch dispersion heated at 95℃, 30 min

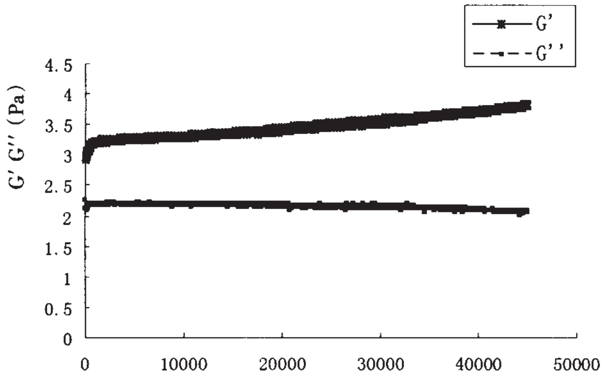

Fig. 4 Storage and loss modulis (frequency 1 HZ, temperature 25℃) as function of time for potato starch. Starch concentration used was 6%

Time sweep is studied in which G′ and G″ are determined as a function of time at fixed (ω) and the temperature. This type of test, often called a gel cure experiment, is well studied for studying structure development in physical gels.

Ellis and Ring[4] showed G′ to be inversely proportional to molecular mass in studies using polydisperse fractions of amylose of molecular mass 4.9×10^5 to 1.1×10^6. Billiaderis[5] argued that for long amylose chains, the initial formation of a few cross-links will retards the chain mobility and subsequent cross-linking. For the starch situation will be even more complex. This is exemplified by the studies on the mixed amylose-amylopectin systems by Parovyori et al [6]. They found that the rate of gelation was faster than for pure amylose alone and that the plateau G′ values obtained were greater for mixtures at amylose: amylopectin ratio less than -3:5 but less than for the mixtures above this ratio. This behavior may be due to the tendency for amylose and amylopectin to segregate at higher concentrations and form two liquid layers each enriched in one or other of the polysaccharides[7,8]. The position of the bimodal separating the one-phase and two-phase regions in the phase diagram will depend on the concentration and molecular mass of both the amylose and amylopectin. In the two-phase region, amylose-amylopectin segregation, and amylose self-association will occur simultaneously, but at low temperatures association will be rapid and complete segregation will be inhibited. Figure 4 shows G′, G″ as a function of time. Potato sample shows the expected behavior with attaining values close to the G′ maximum value at the start of the experiment, and the increase in G′ thereafter was minimal. For potato starch the lower value is due to the lower amylose content and possibly higher amylose molecular mass.

2.3 Gel Strength

Hardness was defined as the peak force exhibited in first bit. Cohesiveness was the quantity necessary to stimulate the strength of the bonds making up the sample. The hardness and cohesiveness for 6% potato starch gel (Figure 5) were 31.3 g and 191.9g·s^{-1}.

Both values were smaller than those of kuzu and lotus starches at the same concentration for the larger molecular mass of potato starch delayed its retrogradation.

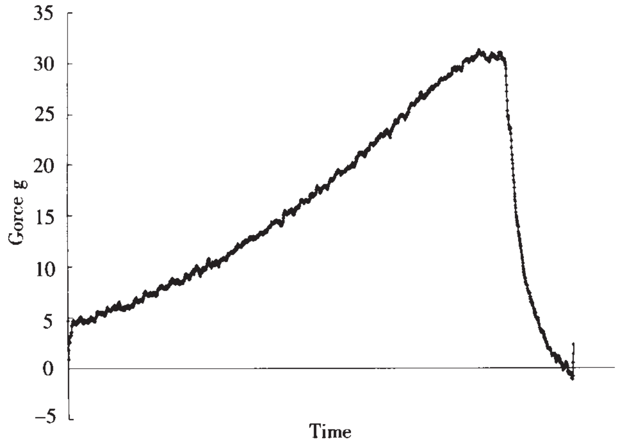

Fig. 5 6% potato starch gel strength

2.4 Differential Scanning Calorimetry

The gelatinization of the potato starch was studied by DSC at water content of 40%(Figure 6). T_0 is the onset temperature, T_p is the peak temperature and T_m is the melting/conclusion temperature, $\triangle T = T_m - T_o$, $\triangle H$ = enthalpy. Here the T_0 was 62.23℃, T_p was 67.21℃, and T_{m}. was 81.31℃, $\triangle H$ was 2.22 J·g^{-1}. There were not too much difference with the results investigated by Marruf *et al*[9].

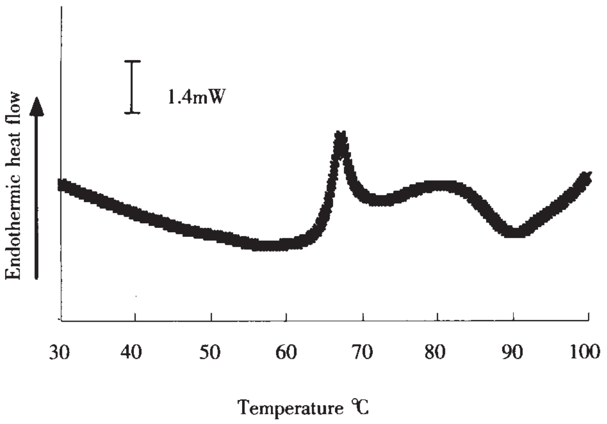

Fig. 6 DSC curve for 1∶3 potato starch∶water. Heating rate∶5℃·min^{-1}

3 Conclusions

The potato starch from southwest China displays particle size ranging from 0.429 –102.3 μm. 6 w/v% potato starch dispersion heated at 95℃ for 30 min shows a shear shinning type fluid at the shear rate up to 800W ·s^{-1}. From frequency and time spectra, G' is higher than G'', but G' is still low. Both G' and G'' were highly dependent on frequency. That means, the 6 w/v% potato starch can form gel but a weak gel. The gel strength and cohesiveness were 31.3 g and 131.9 g·s. The thermal properties of potato starch gelatinization were T_o 62.23℃, T_p67.31℃, and $\triangle H$ 2.22 J·g^{-1} at the starch∶water = 3∶1.

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