Carbohydrate Polymers 92 (2013) 441–447

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Compatibility studies on tea polysaccharide/amylose/water and tea polysaccharide/amylopectin/water

Li Guo[a,b,1], Yu Zhu[a,1], Xian feng Du[a,*]

[a] Key Laboratory of Tea Biochemistry & Biotechnology, Anhui Agricultural University, Hefei 230036, China
[b] Key Laboratory of Cigarette Smoke, Technology Center of Shanghai Tobacco (Group) Corp., Shanghai 200082, China

ARTICLE INFO

Article history:
Received 11 December 2011
Received in revised form 15 August 2012
Accepted 21 September 2012
Available online 28 September 2012

Keywords:
Tea polysaccharide (TPS)
Amylose (Am)
Amylopectin (Ap)
Compatibility
Texture

ABSTRACT

The compatibilities of amylose/tea polysaccharide (Am/TPS) and amylopectin/tea polysaccharide (Ap/TPS) in water were investigated with theoretical calculations and experimental measurements. To achieve this, dilute-solution viscometry (DSV) and high-speed differential scanning calorimetry (hyper-DSC) were used. The compatibility criteria on the basis of Δb_m, ΔB_m, μ, $\Delta[\eta]_m$ and thermodynamic parameters, T_g and ΔT_g were estimated. The data obtained from DSV show that the Am/TPS mixtures with 0.65:0.35, the Ap/TPS mixtures with (a) 0.85:0.15 and (b) 0.75:0.25 at limited moisture are completely miscible. The results were also confirmed using DSC. A texture analyzer was also used to study effects of Am/TPS and Ap/TPS with different weight fractions on the textures of mixed sol. The results show that the firmness, consistency, cohesiveness and index of viscosity of the Am/TPS and Ap/TPS sol increase with the increase of TPS level and that TPS could provide a more desirable physical structure for starch-based foods.

1. Introduction

Starch is a semi-crystalline particle composed of two polysaccharides, amylose (Am) and amylopectin (Ap). Physically, it has both amorphous and crystalline regions (French, 1984). The crystalline regions imparting water insolubility and high viscosity of hot paste consist mainly due to association of short chains of branched Ap with approximately 15–20° of polymerization (DP) in the form of clusters. The amorphous regions providing a site for water uptake, plasticization of granules and chemical reactivity are composed of linear Am with single-stranded helix conformation (Zobel & Stephen, 1995). The functional properties of starch, such as gelatinization, pasting, swelling, viscosity, recrystallization and sol properties are greatly affected by the characterizations of Am and Ap (French, 1984; Gidley & Bulpin, 1989; Leloup, Colonna, & Buleon, 1991; Luallen, 2004; Zobel & Stephen, 1995). Usually these properties are not optimal in native starch, and thus need to be modified by various methods to suit the end product. To achieve this, the synergistic interactions between Am or Ap and some hydrocolloids have been investigated to improve starch thickening, stabilizing and limit its retrogradation. It has been reported that amylose–dextran (Kalichevsky, Orford, & Ring, 1986), amylose–amylopectin (Kalichevsky & Ring, 1987) and amylose–carrageenan (Tecante & Doublier, 2002) mixtures exhibit incompatibility at specific conditions of concentration and composition. Am interacts with galactomannans or κ-carrageenan only if its molecular weight is higher than a critical molecular weight of about 10^6 g/mol (Funami et al., 2005). Mousia, Farhat, Blachot, and Mitchell (2000) determined that two transitions were found in concentrated amylopectin–gelatin mixtures, indicating the existence of two distinct phases. Didem and Jozef (2008) indicated that the mixed inulin–amylopectin systems at limited moisture contents (a_w = 0.33–0.52) was immiscible. Moreover, the addition of polysaccharides like guar gum, locust bean gum, konjac glucomannan, xanthan and galactomannan to starch pastes can increase paste viscosity upon heating and inhibit structural hardening of gel during storage (Chaudemanche & Budtova, 2008; Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Khanna & Tester, 2006; Lii, Tomasik, Hung, & Lai, 2002; Mua & Jackson, 1998). Considering the industrial and nutritional importance of the above effects, starch and polysaccharide mixture are widely used to control and modify food texture. As is widely recognized, ingredient compatibility (or incompatibility) is critical for the control of processability, texture, palatability and stability of the final starch-based foods. If the conditions that favor compatibility of Am or Ap and hydrocolloids can be well-understood and predicted, they can be successfully used in starch-based food applications and their utilization in novel starch-based products will be enhanced.

---

* Corresponding author at: No.130, Western Changjiang Road, Anhui Agricultural University, Hefei City, Anhui Province 230036, China. Tel.: +86 551 5786422; fax: +86 551 5786982.
E-mail address: duxianf@126.com (X.f. Du).

[1] No.130, Western Changjiang Road, Anhui Agricultural University, Hefei City, Anhui Province, China, 230036.

0144-8617/$ – see front matter Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.09.037

Tea polysaccharide (TPS) has been found to be an important water-soluble polysaccharide exhibiting many bioactivities in the late 1980s (Mori, Morita, & Ikeogaya, 1989). Many studies have demonstrated that TPS shows many biological activities such as anti-cancer, anti-mutation, anti-atherosclerotic, anti-radiation damage, anti-oxidant, anti-coagulation, anti-HIV properties, and moderating blood glucose, etc. (Andrea & Michael, 1997; Chen, Zhang, Qu, & Xie, 2008; Chen, Zhang, & Xie, 2004; Yu, Sheng, Xu, An, & Hu, 2007). The addition of TPS to wheat starch was reported to decrease the glass transition temperature and retrogradation rate as well as maintain overall product quality during storage (Zhou, Wang, Zhang, & Du, 2008). So, TPS is attracting more attention in many fields due to its functional properties. In recent years, great advances have been made in structural analysis of TPS in green tea. TPS involves not only β-(1–3) linkages linked rhamnose, glucose and galactose residues but also α-(1–4) linkages and α-(1–6) linkages, and TPS is a glycoprotein having some characteristics of both polysaccharides containing uronic acids and proteins (Chen et al., 2004; Nie, Xie, Fu, Wan, & Yan, 2008; Zhou, Xie, Nie, & Wang, 2004). Lv et al. (2009) showed that TPS is a typical heteropolysaccharide and consisted of mannose, ribose, rhamnose, glucuronic acid, galacturonic acid, glucose, xylose, galactose and arabinose in the molar contents of 16.3, 10.3, 47.1, 5.6, 24.0, 128.4, 25.0, 101.4 and 71.1 μM, respectively. However, the research concerning interactions between Am or Ap and TPS is sparse. In this study, the compatibilities of Am/TPS/water mixture and Ap/TPS/water mixture were investigated using dilute solution viscometry (DSV) and differential scanning calorimetry (DSC). Based on these experimental results, a texture profile analysis of the mixed Am/TPS sol and Ap/TPS sol was obtained. It is expected that such information could allow us to get some insights on their compatibility and on their role in the texture of the blends.

2. Materials and methods

2.1. Materials

Am (A0512) and Ap (A8515) from potato starch were purchased from Sigma–Aldrich (USA). Green tea was purchased from Huangshan city of Anhui Province, China. TPS was isolated and purified according to Guo, Du, Lan, and Liang (2010). Alcohol, phenol, sulfuric acid and polyamide resin (80–100 mesh) were purchased from Nankai University Chemical Co. (Tianjin, China). All other chemicals were of the highest purity commercially available.

2.2. Preparation of the blend solutions

2.2.1. Preparation of the TPS solution

The TPS solution was prepared by dispersing TPS in distilled water at room temperature using a magnetic stirrer and then heating at 70 °C while stirring with a paddle mixer for 30 min. The solution was then centrifuged at 2000 rpm for 30 min to remove any insoluble residues and thus to obtain a clear solution. The concentration of the initial solution was 1 wt%.

2.2.2. Preparation of potato Am and Ap suspensions

Potato Am and Ap dispersions were obtained by dispersing the appropriate powders in distilled water at room temperature using a magnetic stirrer and then heating at 120 °C under 0.1 MPa for 1 h in autoclave. The concentrations of Am and Ap dispersions were 1 wt%. It is worth mentioning that in the preparation of Am solution, Am powder must be slowly added to distilled water with gently stirring for about 12 h at room temperature to obtain a homogenous solution. Otherwise, Am tends to form sticky clumps when large amounts of the samples were added to distilled water.

2.2.3. Preparation of the mixtures

The blend solutions were prepared by mixing 1 wt% TPS solution and 1 wt% Am solution or 1 wt% Ap solution at the required ratios to obtain the blend solutions of various compositions. The blend solutions prepared were used for DSV, hyper-DSC and texture profile analysis.

2.3. Dilute solution viscometry (DSV)

Viscosity measurements of all the blend solutions were made in a thermostatic transparent water bath at 20 ± 0.1 °C using an Ubbelohde dilution viscometer. Ternary solutions were prepared by mixing the appropriate quantity of the two polymer solutions in the weight ratios (W_{Am}:W_{TPS} or W_{AP}:W_{TPS}) of (0.95:0.05), (0.85:0.15), (0.75:0.25) and (0.65:0.35). Dilutions to yield at least four lower concentrations were made by adding the appropriate aliquots of distilled water. Efflux time of the solvent was always above 100 s. Efflux time measurements were recorded after an equilibration time of 15–20 min and were continued until several flow time readings agreed to within ±0.5%. Every value was measured three times and then averaged.

2.3.1. Theoretical background

Dilute solution viscometry (DSV) is a particularly useful method because of its simplicity and low cost. It is based on the classic Huggins equation in polymer/solvent system:

$$\eta_{sp} = [\eta]c + bc^2 \tag{1}$$

where η_{sp} denotes specific viscosity and c is the mass concentration of solution, $[\eta]$ is the intrinsic viscosity reflecting the interaction between polymer and solvent. The interaction parameter b is related to the Huggins coefficient k, which reflects the binary interactions between polymer segments.

(1) $\Delta[\eta]_m$

In polymer1/polymer2/solvent system, Eq. (1) extended by Krigbaum and Wall (1950) can be applied to polymer mixtures in a common solvent. The total concentration ($c = c_1 + c_2$) is introduced. So, the specific viscosity of blends can be expressed as the follow equation:

$$\eta_{spm} = [\eta]_m(c_1 + c_2) + b_m(c_1 + c_2)^2 \tag{2}$$

where subscripts 1, 2 and m represent polymer1, polymer2, and polymer mixtures, respectively.

$$b_m = k_m[\eta]_m^2 \tag{3}$$

$[\eta]_m$ is the weight average of intrinsic viscosity of the two-component polymer mixture. The experimental value of $[\eta]_m^{\exp}$ is determined by extrapolation to infinite dilution of the plot and the value of $b_m^{\exp}$ is obtained from the slope of the plot according to Eq. (2). The criterion $\Delta[\eta]_m$ based on the difference between the experimental and ideal values of $[\eta]_m$ has proposed by Garcia, Melad, Gomez, Figueruelo, and Campos (1999) as follows:

$$\Delta[\eta]_m = [\eta]_m^{\exp} - [\eta]_m^{id} \tag{4}$$

$[\eta]_m^{id}$ is the intrinsic viscosity of the ideal solution introduced as follows:

$$[\eta]_m^{id} = w_1[\eta]_1 + w_2[\eta]_2 \tag{5}$$

where w_1 and w_2 are the weight fractions of the polymer1 and polymer2, respectively. $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of the pure polymer solutions.

This criterion states that compatibility exists if $\Delta[\eta]_m < 0$ and incompatible if $\Delta[\eta]_m > 0$.

(2) Δb_m

The estimation of the compatibility of the polymer blends can be obtained by means of the sign of Δb_m (Chee, 1990; Krigbaum & Wall, 1950).

$$\Delta b_m = b_{12}^{\exp} - b_{12}^{id} \tag{6}$$

Where $b_{12}^{\exp}$ and b_{12}^{id} are the experimental and the ideal viscometric interaction parameter values, respectively.

$$b_{12}^{id} = (b_{11}b_{22})^{1/2} \tag{7}$$

Where b_{11} and b_{22} are determined from pure polymer/solvent systems formed by polymer1 and polymer2 in the solvent, respectively.

The two polymers should be compatible if $\Delta b_m > 0$ and incompatible if $\Delta b_m < 0$.

(3) ΔB_m

According to the ideal blends behavior supposed by Catsiff and Hewett (1962):

$$b_{12}^{id'} = \frac{b_{11} + b_{22}}{2} \tag{8}$$

Chee (1990) proposed a different parameter, ΔB_m, as a simple measure of intermolecular interactions. Chee suggests that the nonideal behavior of blends system can be reflected by the difference between the experimental value $b_{12}^{\exp}$ and the ideal value b_{12}^{id}. It can be expressed as the follow equation:

$$\Delta B_m = b_{12}^{\exp} - b_{12}^{id'} \tag{9}$$

In this case, $\Delta B_m > 0$ signifies compatibility whereas $\Delta B_m < 0$ indicates phase separation and incompatibility.

(4) μ

With these values, Chee (1990) defined a more effective parameter μ to predict polymer–polymer miscibility as follows:

$$\mu = \frac{\Delta B_m}{([\eta]_2 - [\eta]_1)^2} \tag{10}$$

This criterion states that compatibility exists if $\mu > 0$ and incompatibility if $\mu < 0$.

2.4. High-speed differential scanning calorimetry (hyper-DSC)

The dry films used in hyper-DSC were prepared as follows: the blend solutions were cast on clean glass sheets, and dried in a vacuum oven at 50 °C for 24 h and then the resultant membranes were peeled off the glass plate. The thickness of the films was measured by using a digital indicator (Mitutoyo IDC-112CB, Mitutoyo Corp., Kawasaki, Kanagawa, Japan) with an accuracy of ±3 μm. The films were 180–200 μm thick. Prior to the DSC measurements, each sample was kept in the desiccator at 25 °C for one week The moisture content in each sample was estimated from weight loss of sample after drying at 130 °C until a constant weight was reached. Triplicate replicate measurements were performed for each analysis. The moisture contents of all samples were about 5.00%.

The T_gs of the films were performed on a Perkin-Elmer DSC Diamond-1 with an internal coolant (Intercooler 1P). The measurements were carried out under a nitrogen purge gas at a flow rate of 50 mL/min. The instrument was calibrated for temperature and heat flow using indium and zinc as standards at a heating rate of 10 °C/min. A baseline for an empty pan was established for each corresponding heating rate. An empty aluminum pan was used as a reference. Triplicate samples (5.0 ± 0.1 mg, dry basis) were sealed in aluminum pans and scanned under static air over a temperature range of 0–150 °C at a heating rate of 400 °C/min. The inflection point of the step in the heat flow curve in the heating scan was taken as the T_g, which corresponded to the temperature at which one-half of the change in the heat capacity occurred. The onset and endset temperatures were recorded as temperatures at the very beginning and the end of these discontinuities in heat-flow over temperature, respectively (Jara & Pilosof, 2009; Liu, Yu, Liu, Chen, & Li, 2009).

2.5. Measurements of the mixed sol texture

2.5.1. Preparation of Am/TPS sol and Ap/TPS sol

The mixed sol was prepared as follows: the 1 wt% Am/TPS blend solutions with different ratios and the 1 wt% Ap/TPS blend solutions with different ratios were heated and stirred for 0.5 h at 90 °C using a magnetic stirrer (type 85-2, Sile Instrument Factory, Shanghai, China) to ensure complete gelatinization, and then cooled to room temperature to form sol.

2.5.2. Measurements of sol texture

A Texture Analyzer TA-XTplus (Stable Micro Systems, England) was used to measure the force–time curve. In all experiments, samples were compressed under a Back Extrusion Cell (A/BE) with 45 mm disc and extension bar. The TA setting parameters are as follows: Pre-Test Speed was 1.5 mm/s; Test Speed was 2.0 mm/s; Post-Test Speed was 2.0 mm/s; Distance was 20 mm; Trigger Type was Auto-5 g; Tare Mode was Auto; Data Acquisition Rate was 250 pps. Experimental data obtained by using the Texture Analyzer with accompanying computer software (SAS). Every value was measured three times and then averaged.

3. Results and discussion

3.1. DSV analysis

Fig. 1 shows the plot of reduced viscosity vs. concentration for Am/TPS and Ap/TPS at different weight fractions in water. In Fig. 1, the linear relationship has been observed for the polymer mixture over the composition range assayed. Based on the experimentally observed $[\eta]$ for the ternary (poymer1/polymer2/polymer3) systems, the parameters of the compatibility criteria (Δb_m, $\Delta[\eta]_m$, ΔB_m, μ) are listed in Table 1. As illustrated in Fig. 1a, all the plots are linear for the Am/TPS over the composition range assayed. The intrinsic viscosity increases as the fraction of TPS increases indicating the existence of favorable interactions between the two types of chains. When the ratio of mixing was 0.65:0.35, all the compatibility criteria ($\Delta b_m > 0$, $\Delta B_m > 0$, $\mu > 0$, $\Delta[\eta]_m < 0$) are satisfied, indicating good compatibility. All the four parameters ($\Delta b_m < 0$, $\Delta B_m < 0$, $\mu < 0$, $\Delta[\eta]_m > 0$) do not satisfy the compatibility condition for Am/TPS (0.95:0.05; 0.85:0.15 and 0.75:0.25). Fig. 1b shows the same linearities for the combination Ap/TPS. The intrinsic viscosity increases as the fraction of TPS increases. All the compatibility criteria ($\Delta b_m > 0$, $\Delta B_m > 0$, $\mu > 0$, $\Delta[\eta]_m < 0$) are satisfied for compositions 0.85:0.15 and 0.75:0.25, respectively, but not for 0.95:0.05 and 0.65:0.35 ($\Delta b_m < 0$, $\Delta B_m < 0$, $\mu < 0$, $\Delta[\eta]_m > 0$). The above incompatible blends may be due to the lack of hydrogen bonding sites and, hence, the existence of a repulsive interaction between Am or Ap and TPS that leads to incompatibility (Wanchoo & Sharma, 2003).

3.2. Hyper-DSC analysis

3.2.1. T_gs of individual biopolymers

The hyper-DSC curves for the individual biopolymer are shown in Fig. 2. The T_gs of Am and Ap containing about 5% water were detected to be 87.26 °C and 86.43 °C, respectively. On the other

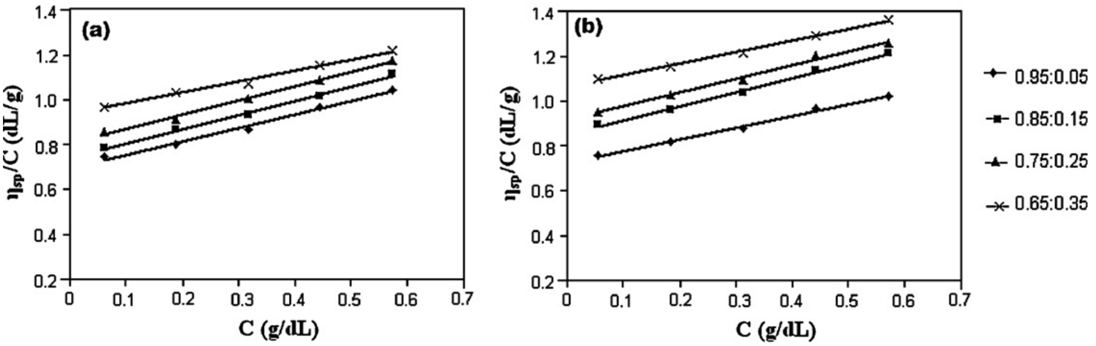

Fig. 1. Plots of reduced viscosity vs. concentration for ternary polymers (a) Am/TPS and (b) Ap/TPS at different weight fractions in water at 20 ± 0.1 °C.

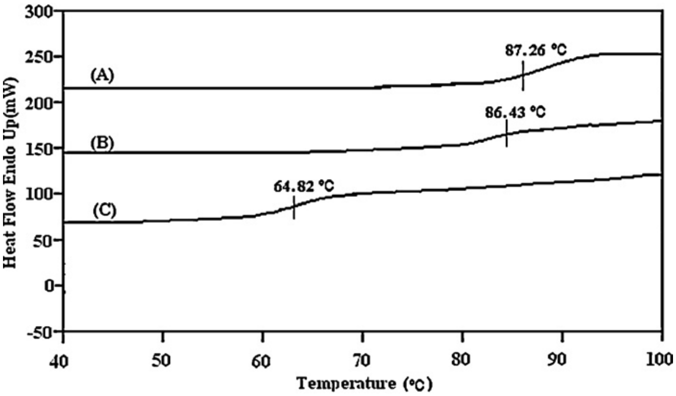

Fig. 2. DSC thermograms of individual biopolymers containing about 5% moisture under heating rate 400 °C/min for (A) Am, (B) Ap and (C) TPS.

hand, T_g value for TPS containing about 5% water was 64.82 °C. It can be seen that T_g of TPS is lower obviously than T_gs of Am and Ap.

3.2.2. T_gs of the mixed Am/TPS and Ap/TPS systems

The glass transition is a critical parameter for amorphous food matrices that control their processability, properties and stability. For a mixing polymer system, the immiscible biopolymer mixtures often possess several T_gs corresponding to the components of the blend. In case of partial compatibility, the T_gs of the components of the blend close to each other due to the effect of mutual diffusion of the mixture components. The closer the T_gs of the components get, the better compatibility of the blend obtains. The complete miscibility a single T_g located between the T_gs of the components is observed (Muraa, Bettinettib, Fauccia, Manderiolia, & Parrini, 1998; Schorsch, Jones, & Norton, 1999). To further estimate accurately the compatibility of the mixing polymer, Song, Hammiche, Pollock, Hourston, and Reading (1996) proposed the following quantification of the deviation:

$$\Delta Tg = T_{ge} - T_{gp} \tag{11}$$

In this equation, T_{ge} is the experimental value of the glass transition and T_{gp} is the predicted glass transition temperature for a mixed system, respectively.

Several equations have been developed to relate the dependence of the T_{gp} of a compatible polymer blend to its composition. One of the most used relations is the Fox equation (Fox & Mulvihill, 1990).

$$T_{gp} = \left(\frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \right)^{-1} \tag{12}$$

In this equation, T_{g1} and T_{g2} are the glass transition temperatures of the individual polymers, w_1 and w_2 are the weight fractions of the individual polymers.

Table 1
The experimental and ideal values of Am/TPS and Ap/TPS at different weight fractions in water by using DSV.

	Am/TPS (wt/wt)				Ap/TPS (wt/wt)			
	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35
$[\eta]_m^{exp}$ (dl g^{-1})	0.696	0.718	0.738	0.794	0.738	0.824	0.868	0.992
b_m^{exp} (dl^2 g^{-2})	0.430	0.600	0.750	0.920	0.750	0.870	0.900	0.670
$[\eta]_m^{id}$ (dl g^{-1})	0.677	0.685	0.746	0.923	0.746	0.874	0.938	0.903
b_m^{id} (dl^2 g^{-2})	0.676	0.820	0.788	0.850	0.788	0.824	0.842	0.792
Δb_{m} (dl^2 g^{-2})	−0.246	−0.220	−0.038	0.070	−0.038	0.046	0.058	−0.122
$\Delta[\eta]_m$ (dl g^{-1})	0.019	0.033	0.008	−0.129	0.008	−0.050	−0.070	0.089
ΔB_m (dl^2 g^{-2})	−0.315	−0.235	−0.065	0.085	−0.065	0.055	0.085	−0.105
μ	−1.909	−1.497	−0.635	0.541	−0.635	0.537	0.830	−1.707

Table 2
T_gs measured for Am/TPS and Ap/TPS with different weight fractions at around 5% moisture content by using Hyper-DSC.

	Am/TPS (wt/wt)				Ap/TPS (wt/wt)			
	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35
T_{ge}	85.21 ± 0.05[a] 62.95 ± 0.03	84.90 ± 0.01 67.57 ± 0.01	83.86 ± 0.01 70.03 ± 0.02	83.34 ± 0.01	86.01 ± 0.01 65.63 ± 0.01	84.90 ± 0.03	83.94 ± 0.01	80.28 ± 0.01 65.63 ± 0.01
T_{gp}	85.78	82.95	80.32	77.83	85.03	82.31	79.78	77.40
ΔT_g	–	–	–	5.51	–	2.59	4.16	–

[a] Data are expressed as means ± standard deviations ($n = 3$).

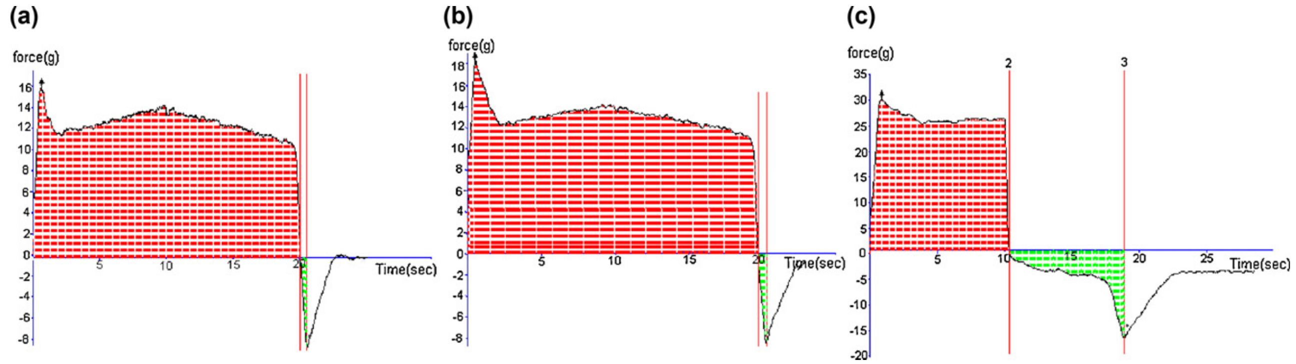

Fig. 3. The texture drawing of 1% biopolymer sol for (a)Am, (b) Ap and (c) TPS.

Table 3
Texture characteristic of 1% individual biopolymer gel.

	Am	Ap	TPS
Firmness (g)	15.949 ± 0.349	18.192 ± 0.057	30.086 ± 0.175
Consistency (gsec)	214.901 ± 0.355	217.006 ± 0.508	257.440 ± 0.598
Cohesiveness (g)	10.820 ± 0.464	11.074 ± 0.201	18.122 ± 0.207
Index of Viscosity (gsec)	2.670 ± 0.590	3.226 ± 0.262	39.231 ± 0.429

A fully compatible polymer has a very small ΔT_g value, close to zero, while a partial compatibility causes a larger ΔT_g value, i.e. 10–40 °C approximately (Song et al., 1996).

Table 2 shows T_gs of mixed Am/TPS and Ap/TPS systems with (a) 0.95:0.05, (b) 0.85:0.15, (c) 0.75:0.25, and (d) 0.65:0.35 at 5% moisture content. In terms of the mixed Am/TPS system with 0.95:0.05, 0.85:0.15 and 0.75:0.25, there are two T_gs indicating that the mixed systems are incomplete miscibility at limited moisture content. The different ratios of the Am/TPS mixtures (0.85:0.15; 0.75:0.25) except for the ratio (0.95:0.05) locate between the T_gs of Am and TPS, and as the concentration of TPS increased, it has positive effect on the miscibility of the mixed system. This suggests that the Am/TPS mixtures (0.85:0.15; 0.75:0.25) are partial compatibility. There is only one T_g indicating that the mixed systems are complete miscibility at limited moisture content when the ratio of the Am/TPS mixtures is 0.65:0.35. Similarly, the different ratios of the Ap/TPS mixtures (0.95:0.05; 0.65:0.35) locate between the T_gs of Ap and TPS, which indicates the mixed systems are partial compatibility at limited moisture content. There is only one T_g indicating that the mixed systems are complete miscibility at limited moisture content when the ratios of the Ap/TPS mixtures are 0.85:0.15 and 0.75:0.25, respectively. Table 2 also shows ΔT_g values calculated for the Am/TPS mixtures with 0.65:0.35 and the Ap/TPS mixtures with 0.85:0.15 and 0.75:0.25 at 5% moisture content, respectively. Clearly, three ΔT_g values are less than 10 and close to T_{gp}s calculated by Fox equation, which provides information that the Am/TPS and Ap/TPS mixtures with moderate ratios were perfectly compatible at limited moisture content. Moreover, the addition of TPS has obvious plasticizing effects on Am and Ap, and this effect is related with the concentration of TPS. This result is almost in agreement with previous results determined by using DSV. In our previous experiment (Guo et al., 2010), TPS determined shows such the configuration as hyperbranched and spherical molecular. Furthermore, TPS involves not only β-(1–3) linkages but also α-(1–4) linkages and α-(1–6) linkages (Chen et al., 2004). Therefore, with regard to the TPS properties, TPS can increase plasticization and molecular movement of the Am and Ap chains, offer high rotational degrees of freedom of the mixed Am/TPS and Ap/TPS system and decrease intermolecular distances, thereby reducing the interfacial tension and increasing the compatibility between TPS and Am or Ap (Chattopadhyay, 2000; Wanchoo & Sharma, 2003).

3.3. *Texture characteristic analysis*

Based on the experimental results determined by DSV and DSC, the texture characteristics of Am, Ap, TPS as well as the mixed Am/TPS and Ap/TPS sol were analyzed by using a texture analyzer. The texture drawing and parameters for the individual biopolymer are shown in Fig. 3 and Table 3. Four parameters were used to describe texture characteristic of sol. When a 5 g surface trigger is attained (i.e. the point at which the disc's lower surface is in full contact with the product), the disc proceeds to penetrate to a depth of 20 mm. At this point (most likely to be the maximum force), the probe returns to its original position. The 'peak' or maximum force is taken as a measurement of firmness. The higher the value is, the firmer the sample is. The area of the curve up to this point is taken as a measurement of consistency. The higher the value is, the thicker the consistency of the sample is. The negative region of the graph, produced on probe return, is as a result of the weight of sample which is lifted primarily on the upper surface of the disc on return, i.e. due to back extrusion and hence gives again an indication of consistency/resistance to flow off the disc. The maximum negative force is taken as an indication of the cohesiveness of the sample. The more negative the value is, the more cohesive the sample is. The area of the negative region of the curve may be referred to as the 'Index of Viscosity'-the higher value indicates the more resistance to withdraw the sample (TA.XTplus Texture Analyser-Technical Description & Service Manual, 2010). As listed in Table 3, the firmness, consistency, cohesiveness and index of viscosity of TPS sol are significantly higher than that of Am and Ap sol. The changes of the textures of the Am/TPS and Ap/TPS sol with (a) 0.95:0.05, (b) 0.85:0.15, (c) 0.75:0.25 and (d)

Table 4
Effects of Am/TPS and Ap/TPS with different weight fractions on the textures of mixed gel.

	Am/TPS (wt/wt)				Ap/TPS (wt/wt)			
	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35	0.95:0.05	0.85:0.15	0.75:0.25	0.65:0.35
Firmness (g)	16.338 ± 0.386	16.367 ± 0.246	17.755 ± 0.316	20.835 ± 0.246	17.216 ± 0.001	17.673 ± 0.246	18.738 ± 0.316	21.327 ± 0.246
Consistency(gsec)	217.030 ± 0.146	217.373 ± 0.656	217.918 ± 0.072	218.566 ± 0.788	217.151 ± 0.952	217.646 ± 0.054	218.361 ± 0.143	218.843 ± 0.942
Cohesiveness (g)	11.278 ± 0.176	12.543 ± 0.176	13.421 ± 0.057	14.124 ± 0.001	11.630 ± 0.105	12.754 ± 0.176	12.976 ± 0.088	14.546 ± 0.211
Index of Viscosity (gsec)	2.730 ± 0.184	3.902 ± 0.174	4.796 ± 0.295	7.106 ± 0.732	3.351 ± 0.121	3.614 ± 0.248	4.188 ± 0.685	5.908 ± 0.237

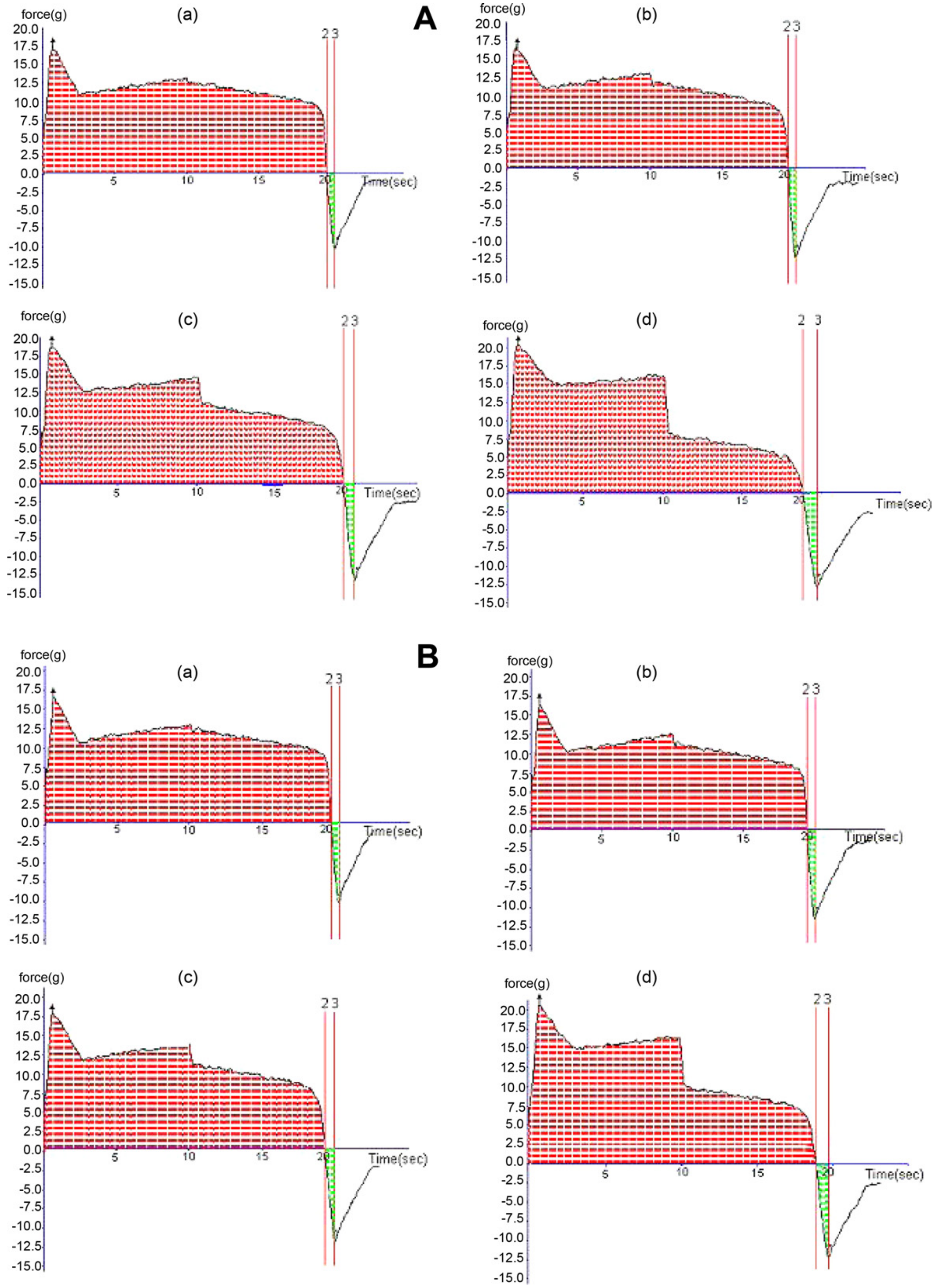

Fig. 4. Effects of (A) Am/TPS and (B) Ap/TPS with different weight fractions on the textures of mixed sol: (a) 0.95:0.05, (b) 0.85:0.15, (c) 0.75:0.25 and (d) 0.65:0.35.

0.65:0.35 are showed in Fig. 4. The corresponding data determined are listed in Table 4. It can be seen that the texture parameters of the Am/TPS and Ap/TPS sol generally increase with the increase of TPS level. Increased sol firmness of Am and Ap by TPS may therefore be attributed to the formation of a strong Am and Ap sol matrix network via changes of conformational ordering and intermolecular association of Am and Ap chains probably by creating more junction zones on Am and Ap chains (Ong & Blanshard, 1995; Verbekena, Thas, & Dewettinck, 2004). By promoting polymer–polymer association, TPS can markedly change the conformational ordering and intermolecular association of starch polymers. This greatly affects the physical and mechanical properties of starch sol. Table 4 shows that the other textural properties, consistency, cohesiveness and index of viscosity also followed a similar trend as exhibited for sol firmness in the presence of TPS (Anil, Somathilaka, & Harold, 2007; Sudhir, Chandralekha, Demappa, Jayaraju, & Keshavayya, 2009).

4. Conclusions

Characterization of the compatibility of polymer blends is important because properties depend on the compatibility of polymers at the molecular level. Polymer–polymer interactions in blends were studied by dilute-solution viscometry (DSV) and high-speed differential scanning calorimetry (hyper-DSC) techniques. From our observations it is clear that the Am/TPS mixtures at a ratio of 0.65:0.35, and Ap/TPS mixtures at ratios of (a) 0.85:0.15 and (b) 0.75:0.25 satisfy all the miscibility/compatibility criteria determined by using DSV and Hyper-DSC. This observation is consistent with the presence of the hydrogen bonding sites present in the structure of these polymers. While the Am/TPS mixtures with (a) 0.95:0.05, (b) 0.85:0.15 and (c) 0.75:0.25, the Ap/TPS mixtures with (a) 0.95:0.05 and (b) 0.65:0.35 do not satisfy all the miscibility/compatibility criterion, which may be due to absence of hydrogen bonding sites in this system. This suggests that in addition to the Am and Ap content the intermolecular association of starch and polymer also affects the textural properties of the starch based sol. The experimental results indicate that the addition of TPS can combine compatibly with Am and Ap to form the undivided network structure, high cohesiveness and viscoelasticity, which makes a great tasting product. So, the addition of TPS is an efficient method for providing a more desirable physical structure for starch-based foods.

Acknowledgments

This research has been supported by the Youth Natural Science Foundation of Department of Science and Technology of Anhui Province, China (grant no. 10040606Q23) and the National Natural Science Foundation of China (grant no. 31171655). We thank Key Laboratory of Cigarette Smoke, Technology Center of Shanghai Tobacco (Group) Corp. for instrument and technology supports.

References

Andrea, R. P., & Michael, H. G. (1997). Antioxidant properties of catechins and green tea extracts in model food emulsions. *Journal of Agricultural and Food Chemistry*, *45*, 4267–4270.

Anil, G., Somathilaka, R., & Harold, C. (2007). Thermal, pasting, and gelling properties of wheat and potato starches in the presence of sucrose, glucose, glycerol, and hydroxypropyl β-cyclodextrin. *Carbohydrate Polymers*, *70*, 112–122.

Catsiff, R. H. E., & Hewett, W. A. (1962). The interaction of two dissimilar polymers insolution. *Journal of Applied Polymer Science*, *6*, 30–32.

Chattopadhyay, S. (2000). Compatibility studies on solution of polymer blends by viscometric and phase-separation technique. *Journal of Applied Polymer Science*, *4*, 880–889.

Chaudemanche, C., & Budtova, T. (2008). Mixtures of pregelatinised maize starch and κ-carrageenan: Compatibility, rheology and gelation. *Carbohydrate Polymers*, *72*, 579–589.

Chee, K. K. (1990). Determination of polymer–polymer miscibility by viscometry. *European Polymer Journal*, *26*, 423–426.

Chen, H. X., Zhang, M., & Xie, B. J. (2004). Quantification of uronic acids in tea polysaccharide conjugates and their antioxidant properties. *Journal of Agricultural and Food Chemistry*, *52*, 3333–3336.

Chen, H. X., Zhang, M., Qu, Z. S., & Xie, B. J. (2008). Antioxidant activities of different fractions of polysaccharide conjugates from green tea (*Camellia sinensis*). *Food Chemistry*, *106*, 559–563.

Closs, C. B., Conde-Petit, B., Roberts, I. D., Tolstoguzov, V. B., & Escher, F. (1999). Phase separation and rheology of aqueous starch/galactomannan systems. *Carbohydrate Polymers*, *39*, 67–77.

Didem, Z. I., & Jozef, L. K. (2008). Theoretical analysis of predictive compatibility of carbohydrate polymers—Software calculations for inulin–amylopectin systems. *Carbohydrate Polymers*, *72*, 52–59.

French, D. (1984). Organization of starch granules. In R. Whistler, J. N. Bemiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 183–256). Orlando: Academic Press.

Fox, P. F., & Mulvihill, D. M. (1990). In P. Harris (Ed.), *Food gels* (pp. 121–173). London: Elsevier Applied Science Publishers.

Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I., & Nishinari, K. (2005). Effects of non-ionic polysaccharides on the gelatinization and retrogradation behaviour of wheat starch. *Food Hydrocolloids*, *19*, 1–13.

Garcia, R., Melad, O., Gomez, C. M., Figueruelo, J. E., & Campos, A. (1999). Viscometric study on the compatibility of polymer–polymer mixtures in solution. *European Polymer Journal*, *35*, 47–55.

Gidley, M. J., & Bulpin, P. V. (1989). Aggregation of amylose in aqueous systems: The effect of chain length on phase behavior and aggregation kinetics. *Macromolecules*, *22*, 341–346.

Guo, L., Du, X. F., Lan, J., & Liang, Q. (2010). Study on molecular structural characteristics of tea polysaccharide. *International Journal of Biological Macromolecules*, *47*, 244–249.

Jara, F. L., & Pilosof, A. M. R. (2009). Glass transition temperature of protein/polysaccharide co-dried mixtures as affected by the extent and morphology of phase separation. *Thermochimica Acta*, *487*, 65–73.

Kalichevsky, M. T., Orford, P. D., & Ring, S. G. (1986). The incompatibility of concentrated aqueous solutions of dextran and amylose and its effects on amylose gelation. *Carbohydrate Polymers*, *6*, 145–154.

Kalichevsky, M. T., & Ring, S. G. (1987). Incompatibility of amylose and amylopectin in aqueous solution. *Carbohydrate Research*, *162*, 323–328.

Khanna, S., & Tester, R. F. (2006). Influence of purified konjac glucomannan on the gelatinization and retrogradation properties of maize and potato starches. *Food Hydrocolloids*, *20*, 567–576.

Krigbaum, W. R., & Wall, F. T. (1950). Viscosities of binary polymeric mixtures. *Journal of Polymer Science*, *5*(4), 505–514.

Leloup, V. M., Colonna, P., & Buleon, A. (1991). Influence of amylose–amylopectin ratio on gel properties. *Journal of Cereal Science*, *13*, 1–13.

Lii, C. Y., Tomasik, P., Hung, W. L., & Lai, V. M. F. (2002). Polysaccharide–polysaccharide interactions in pastes. *Polish Journal of Food and Nutrition Sciences*, *11*, 29–33.

Liu, P., Yu, L., Liu, H. S., Chen, L., & Li, L. (2009). Glass transition temperature of starch studied by a high-speed DSC. *Carbohydrate Polymers*, *77*, 250–253.

Luallen, T. (2004). Utilizing starches in product development. In A. C. Eliassion (Ed.), *Starch in food: Structure, function and applications* (pp. 393–424). Cambridge and New York: Woodhead Publishing Limited and CRC Press LLC.

Lv, Y., Yang, X. B., Zhao, Y., Ruan, Y., Yang, Y., & Wang, Z. Z. (2009). Separation and quantification of component monosaccharides of the tea polysaccharides from *Gynostemma pentaphyllum* by HPLC with indirect UV detection. *Food Chemistry*, *112*, 742–746.

Mori, M., Morita, N., & Ikeogaya, K. (1989). Polysaccharides from tea for manufacture of hypoglycemics antidiabetics and health foods. *Chemical Abstracts*, *111*, 140472.

Mousia, Z., Farhat, I. A., Blachot, J. F., & Mitchell, J. R. (2000). Effect of water partitioning on the glass-transition behaviour of phase separated amylopectin–gelatin mixtures. *Polymer*, *41*, 1841–1848.

Mua, J. P., & Jackson, D. S. (1998). Retrogradation and gel textural attributes of corn starch amylose and amylopectin fractions. *Journal of Cereal Science*, *27*, 157–166.

Muraa, P., Bettinettib, G. P., Fauccia, M. T., Manderiolia, A., & Parrini, P. L. (1998). Differential scanning calorimetry in compatibility testing of picotamide with pharmaceutical excipients. *Thermochimica Acta*, *321*, 59–65.

Nie, S. P., Xie, M. Y., Fu, Z. H., Wan, Y. Q., & Yan, A. P. (2008). Study on the purification and chemical compositions of tea glycoprotein. *Carbohydrate Polymers*, *71*, 626–633.

Ong, M. H., & Blanshard, J. M. V. (1995). Texture determinants in cooked, parboiled rice. I: Rice starch amylose and the fine stucture of amylopectin. *Journal of Cereal Science*, *21*, 251–260.

Schorsch, C., Jones, M. G., & Norton, I. T. (1999). Thermodynamic incompatibility and microstructure of milk protein/locust bean gum/sucrose systems. *Food Hydrocolloids*, *13*, 89–99.

Song, M., Hammiche, A., Pollock, H. M., Hourston, D. J., & Reading, M. (1996). Modulated differential scanning calorimetry: 4. Compatibility and glass transition behaviour in poly (methyl methacrylate) and poly (epichlorohydrin) blends. *Polymer*, *37*, 5661–5665.

Sudhir, R. I., Chandralekha, F., Demappa, T., Jayaraju, J., & Keshavayya, J. (2009). Compatibility studies of HPMC/PEG blends in water by viscosity, density, refractive index and ultrasonic velocity method. *Carbohydrate Polymers*, *75*, 484–488.

Tecante, A., & Doublier, J. L. (2002). Rheological investigation of the interaction between amylose and κ-carrageenan. *Carbohydrate Polymers*, *49*, 177–183.

Verbekena, D., Thas, O., & Dewettinck, K. (2004). Textural properties of gelled dairy desserts containing κ-carrageenan and starch. *Food Hydrocolloids*, *18*, 817–823.

Wanchoo, R. K., & Sharma, P. K. (2003). Viscometric study on the compatibility of some water-soluble polymer–polymer mixtures. *European Polymer Journal*, *39*, 1481–1490.

Yu, F., Sheng, J. C., Xu, J., An, X. X., & Hu, Q. H. (2007). Antioxidant activities of crude tea polyphenols, polysaccharides and proteins of selenium-enriched tea and regular green tea. *European Food Research and Technology*, *225*, 843–848.

Zhou, P., Xie, M. Y., Nie, S. P., & Wang, X. R. (2004). Primary structure and configuration of tea polysaccharide. *Science in China, Series C: Life Science*, *47*, 416–424.

Zhou, Y. B., Wang, D. F., Zhang, L., & Du, X. F. (2008). Effect of polysaccharides on gelatinization and retrogradation of wheat starch. *Food Hydrocolloids*, *22*, 505–512.

Zobel, H. F., & Stephen, A. M. (1995). Chapter 2: Starch: Structure, analysis and application. In A. M. Stephen (Ed.), *Food polysaccharides and their applications* (pp. 19–66). New York: Marcel Dekker.