



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

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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.

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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.

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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 μ M, 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 $\pm 0.5\%$. 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:

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

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:

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

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

$$b_m = k_m[\eta]_m^2 \quad (3)$$

$[\eta]_m$ is the weight average of intrinsic viscosity of the two-component polymer mixture. The experimental value of $[\eta]_m^{\text{exp}}$ 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:

$$\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}} \quad (4)$$

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

$$[\eta]_m^{\text{id}} = w_1[\eta]_1 + w_2[\eta]_2 \quad (5)$$

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 $\Delta[\eta]_m > 0$.

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