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# Influence of xyloglucan on gelatinization and retrogradation of tapioca starch

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## Abstract

Dynamic and steady shear rheometry and differential scanning calorimetry (DSC) were used to investigate effects of xyloglucan (XG) on gelatinization and retrogradation of tapioca starch (TS). The viscosity of TS/XG pastes immediately after gelatinization increased with increasing XG content at the total polysaccharide concentration of 3.5%. Gelatinized TS alone showed pseudoplastic flow at low shear rates and dilatant behavior at higher shear rates (about $>1\ \mathrm{s}^{-1}$), while mixtures with XG did not show dilatancy. Mechanical spectra of TS pastes containing XG were more liquid-like than those of TS pastes without XG. XG provides shear stability to the TS during storage. Increases in dynamic moduli during storage at 5 °C were suppressed in the presence of XG. In contrast, the retrogradation ratio determined based on DSC increased more rapidly in the presence of XG. These results suggest that XG forms a continuous liquid phase in a mixture to impart better mechanical stability during storage but to accelerate re-ordering of starch polysaccharides by effectively reducing the amount of water available for starch.

*Keywords:* Xyloglucan; Tapioca starch; Gelatinization; Retrogradation; Storage stability

## 1. Introduction

Tapioca starch (TS), produced from cassava roots, is a favorable thickener in food industries due to its high viscosity, clear appearance, and low production cost, compared to other starches, especially in Southeast Asia (Rapaille & Vanhemelrijck, 1997). In food production, long shelf-life stability is needed during distribution and household storage. However, starch pastes often suffer from low stability against shear or other mechanical stimuli. It is usually the case that the viscosity of a starch paste decreases when mechanically disturbed. This drives the industries to use a relatively high concentration of starch compared to other hydrocolloids (Sriroth & Piyachomkwan, 2000). Additionally, although tapioca starch itself has traditionally been used as a thickener, the slimy texture can be regarded as somewhat less than desirable. This textural instability during storage is the driving force to modify the starch for improving the shelf life of product using tapioca starch as a thickener.

Incorporation of a proper amount of hydrocolloids may improve textural properties and stability of tapioca starch in food products. Blending of starches with other biopolymers is a well-known technique to modify texture or maintain desirable texture during a long storage period (Lee, Baek, Cha, Park, & Lim, 2002; Tester & Sommerville, 2003). When a starch/hydrocolloid mixture is used as a texture modifier, understanding of its rheological and thermal properties is important. Thus, various studies on rheological and thermal properties of mixtures between starches and hydrocolloids have been reported (Shi & BeMiller, 2002; Sudhakar, Singhal, & Kulkarni, 1995). In general, the viscosity of a mixed system is greatly higher than starch alone since most biopolymers are strongly hydrophilic and compete with starch for water (Christianson, Hodge, Osborne, & Detroy, 1981; Sudhakar, Singhal, & Kulkarni, 1996). The extent of

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starch granule swelling or melting of crystalline parts during gelatinization is influenced by the presence of hydrocolloids and synergistic interactions between hydrocolloids and starch may be anticipated (Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Shi & BeMiller, 2002). Retrogradation of the starch can be altered depending on the type and concentration of individual components in the mixed systems during storage. For example, the freeze-thaw stability of sago starch containing galactomannan was improved by preventing the aggregation of amylose and amylopectin (Ahmad & Williams, 2001) while xyloglucan molecules prevent the gelatinized corn starch structure reordering after 7 days of storage by decreasing the retrogradation and syneresis of the corn starch pastes (Yoshimura, Takaya, & Nishinari, 1999).

From viewpoints of texture and stability modification, xyloglucan (XG) is an interesting hydrocolloid (Nishinari, Zhang, & Ikeda, 2000). XG has a β-(1–4) linked D-glucan backbone that is partially substituted at the O-6 position of its glucopyranosyl residues with α-D-xylopyranose. Some of the xylose residues are further substituted at the O-2 position with β-D-galactopyranose (Nishinari, Yamatoya, & Shirakawa, 2000). XG exhibits a high water holding capacity and good stability to heat, acids and shear. In food industry, XG is widely used as a thickener, stabilizer, fat replacer, or starch modifier in many products for example ice cream, dressing, mayonnaise, noodles, stew, etc. to improve rheological and thermal properties of products (Nishinari et al., 2000). It has been shown that an addition of XG extracted from the seeds of tamarind or *Hymenaea courbaril* into corn starch yielded high paste viscosity but it could have no influence on pasting temperature (Freitas, Gorin, Neves, & Sierakowski, 2003) or slightly lower (Prabhanjan & Ali, 1995) or increase the pasting temperature (Yoshimura et al., 1999). However, gelatinization and retrogradation behavior of TS in the presence of XG has rarely been investigated. The objectives of this study were to study the effect of XG on rheological and thermal properties of TS to obtain fundamental knowledge needed for further food applications in product and process development.

## 2. Materials and methods

### 2.1. Materials

Tapioca starch (TS) was purchased from a manufacturer in Chonburi, Eastern Thailand (lot no. 1403). The moisture and amylose contents of the starch were 12.1 and 22.0% (dry weight basis) determined by hot air oven method at 105 °C (AOAC, 1995) and HPSEC (modified method of Govindasamy, Oates, & Wong, 1992), respectively. Tamarind seed xyloglucan (XG) was a gift from Dainippon Pharmaceutical Co., Ltd (Osaka, Japan). The moisture content of the xyloglucan was 6.4% w/w. The samples were used without further purification.

### 2.2. Dynamic viscoelasticity measurements

#### 2.2.1. Pasting behavior

Changes in dynamic mechanical properties during a heating/cooling process of TS/XG mixtures were monitored using a stress-controlled rheometer (RheoStress1, Haake, Germany). Three mixing ratios (TS/XG = 7/3, 6/4 and 5/5) were chosen at the total polysaccharide concentration of 3.5% w/w in order to avoid sedimentation of starch granules during the experiments. TS and XG powders were dispersed together into distilled water at room temperature (25 °C), loaded into the cup of a double gap cylinder test fixture (DG41-Ti, Haake, Germany) preset at 50 °C, and immediately covered with silicone oil to prevent water loss during heating–cooling cycle. Dynamic moduli of the samples were measured during temperature ramp from 50 to 95 °C at the rate of 0.5 °C/min and successive cooling down to 5 °C at the rate of −0.5 °C/min. The storage modulus ($G'$) and loss modulus ($G''$) were determined using a strain-controlled mode with a strain of 1% at a frequency of 10 rad/s. Stress sweep measurements were performed to confirm that data were obtained within the linear viscoelastic strain region.

#### 2.2.2. Evolution of mechanical spectra during storage

Weighed amounts of TS and XG were dispersed into distilled water at the total polysaccharide content of 3.5% w/w with five mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, and 6/4). Sodium azide (0.04% w/w) was added to prevent microbial spoilage. The mixtures were stirred using a magnetic stirrer for 1 h at room temperature (25 °C), heated in a boiling-water bath, and then further stirred for 30 min while the sample temperature was maintained at 95–98 °C. An aliquot was divided into 10 ml screw-cap glass tubes for storage test and the sample tubes were cooled down in an iced-water bath to 25 °C immediately without further stirring and kept in refrigerated room at 5 °C. After pre-specified storage periods at 5 °C, measurements of frequency dependence of dynamic moduli were performed at 5 °C using a Rheometric Fluids Spectrometer (RFSII, Rheometrics Co. Ltd, USA) with a parallel plate test fixture (50 mm diameter, 1.5 mm gap) in the frequency range from 0.1 to 100 rad/s. Values of strain used for all experiments were confirmed to be within the linear viscoelastic regions determined based on strain sweep experiments. The experiments were done in duplicate.

### 2.3. Steady shear viscosity measurements

TS and XG (3.5% total polysaccharide content) were weighed and mixed together at five mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, and 6/4) in distilled water. The total polysaccharide content of all samples was selected to be 3.5% to generate sufficient torque responses for