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Effect of Xanthan Gum on the Quality of Syrup Thickened by Modified Starch during Heating and Storage

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ABSTRACT

In heating during production and in storage, the reduction in the viscosity of fruit syrup stabilized by starch is a problem in the food industry due to starch degradation, especially in low pH systems. The influence of xanthan gum (Xan) on the rheological properties of syrups with different heating times and during storage was investigated. Blueberry syrups were prepared using 4% total concentration of polysaccharides with different mixing ratios of modified tapioca starch (MTS) and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). The syrups were heated to 90°C and further heated for 20, 40, 60 and 80 min. All formulations with different heating times exhibited lower viscosity with shear rate. Viscosities of the syrups containing Xan were higher than those without Xan. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) obtained from heating at 90°C for 40 min was selected to evaluate the quality change during storage according to the highest sensory scores of thickness and overall liking. The syrup with 0.2% Xan substitution for MTS exhibited higher viscosity and a lower rate of viscosity reduction than that without Xan. Zero-order equations were used for shelf life evaluation of the syrups. Overall liking scores of the syrup with 0.2% Xan before and after storage for 16 wk were not significantly ($p>0.05$) different and exhibited higher scores than those without Xan. The results suggested that Xan could be used in fruit syrup to enhance quality and stability in terms of viscosity during heating and storage.

Keywords: shelf life, hydrocolloid, storage test, viscosity, zero-order reaction

INTRODUCTION

Fruit syrup is one of the important ingredients that can be created to have different flavor, taste, color and texture properties using different sugars, acids, fruit flavors, fruit purée and colorants including polysaccharides. In the food industry, many types of polysaccharides are used in syrup as a thickening agent to modify the rheological properties of the products (Bedi *et al.*, 2005) and hence increase the stability. Starch is one of the polysaccharides widely used for enhancing the viscosity. However, starch-based syrup is subjected to both shear stress and thermal treatment during processing, resulting in the breakdown of starch molecules. The viscosity of the syrup is one of the important quality parameters to be considered in food applications and is observed to decrease after the heat and shear treatments leading to instability of viscosity during storage (Temsiripong *et al.*, 2005; Biliaderis, 2009).

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Hydrocolloids are one of the ingredients used in starch-based products to enhance quality and stability, including the shelf life, in terms of viscosity stability. The incorporation of hydrocolloids is a well-known technique used to improve or maintain desirable textural properties and the stability of most starch-based products during long storage periods, by controlling rheological properties in the continuous phase and the textural properties of product (Yoshimura *et al*., 1998; Mandala *et al*., 2002; Temsiripong *et al*., 2005; Pongsawatmanit and Srijunthongsiri, 2008). Xanthan gum is used in the food industry for improving the stability of many food products. It is a unique hydrocolloid, providing an excellent stability in thermal and acid systems (Morris, 1995). There are many foods that use a mixture of starch and xanthan gum to improve the product quality (Chantaro and Pongsawatmanit, 2010). For example, the structure of strawberry dessert sauces thickened with potato starch and xanthan gum provided stable sensory and textural properties after a 3-month storage period (Sikora *et al*., 2001).

Therefore, blueberry syrup stabilized by modified tapioca starch (MTS) was used as a food model for investigation. The objective of this study was to determine the effect of heating time on the viscosity of blueberry syrup containing different combinations of MTS and xanthan gum (Xan). The quality of selected syrups during storage was also determined. The modified starch used as a stabilizer and/or thickener in this study was hydroxypropyl distarch phosphate (HDP; E1442).

MATERIALS AND METHODS

Materials

MTS (Siam Modified Starch, Thailand) as hydroxypropyl distarch phosphate (HDP; E1442) and commercial Xan (Dessen Biochemical, China) were used in this study. Commercial sucrose, 42% dextrose equivalent (DE) glucose syrup, citric acid monohydrated, blueberry flavor and food colorants were purchased from local suppliers. Frozen blueberry purée (total soluble solids (TSS) = 10.6°Brix, pH = 3.46) prepared by the individual quick frozen (IQF) process was used. Oriented polyamide (OPA) film (360 ± 5 mm length, 240 ± 5 mm width, 100 ± 10 μm thickness) was used for packing the syrup during the storage test.

Effect of heating time on quality of blueberry syrup

Blueberry syrup preparation for various heating times

Blueberry syrup samples containing 4% total concentration of polysaccharides were prepared with different mixing ratios of MTS and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). Each formulation consisted of other ingredients with fixed percentages: 54% sugars (glucose syrup and sucrose), 10% blueberry purée, 31.2% water and 0.8% citric acid, sorbic acid, color and flavor.

A batch of blueberry syrup (2 kg) was prepared for each formulation. MTS was added into water for preparing the MTS dispersion. For MTS/Xan mixtures, Xan was mixed with a part of the sucrose from the formulation, dispersed in the water and stirred continuously for 1 h, before adding the MTS. Then, fruit purée, sugar, glucose syrup and color were added and mixed using a stirrer for a further 1 h at room temperature to hydrate the starch and hydrocolloid.

Each mixture was heated using a water bath and stirred until the temperature of the syrup reached 90°C. The citric acid and sorbic acid were added when the syrup temperature reached about 70°C. Finally, the flavor was added at 90°C. Each syrup formulation was heated further for 80 min and sampled for quality evaluation at 20, 40, 60 and 80 min of heating time.

Quality measurement of blueberry syrup

The apparent viscosity of a sample of the prepared blueberry syrup (16 mL) from each heating time at 90°C was measured as a function of shear rate and ranged from 2.5 to 62.5 s^{-1} at 25 ± 0.1°C using a rotational viscometer (DV-III, Brookfield-RVT) with coaxial cylinder geometry on a small sample adapter and an SC4-29 spindle. Sample temperatures were kept constant for at least 5 min before starting measurement. The flow characteristics of the syrups were evaluated.

Blueberry syrups with and without Xan with selected heating times at 90°C were analyzed for total soluble solids using a refractometer (Atago, Japan), pH with a pH meter and water activity using a dew point hygrometer, Aqualab Series 3B (Decagon Devices, Pullman, Washington, USA) at 25°C. The sensory evaluation of the products with and without Xan was performed using 30 untrained panelists for acceptance testing. Each syrup sample (20 g) with and without Xan was served in a cup with pieces of bread. The panel members were asked to rate the liking of quality attributes according to appearance, color, odor, thickness and overall liking using a 9-point hedonic scale, with 1 = dislike extremely to 9 = like extremely.

Quality change of blueberry syrup during storage

The blueberry syrup formulation containing Xan that had a good quality in terms of viscosity and a sensory evaluation score was selected for appraisal of quality change during storage. Twenty kilograms of each syrup preparation with and without Xan (as control) were prepared by heating the syrups for 40 min at 90°C, hot filling into an OPA bag (500 g), hermetically sealing, cooling and keeping at ambient temperature (average 30±3°C) for 16 wk. The syrups were sampled for quality measurement after certain periods of storage time. The viscosity, total soluble solids and pH values were determined using the methods mentioned above.

Sensory evaluation of the product with and without Xan before and after storage for 16 wk was performed using 30 untrained panelists for acceptance testing, using the procedure described above.

Statistical analysis

All measurements were performed with at least two replications. Mean values ± standard deviation were reported. Analysis of variance (ANOVA) was used to determine any significant differences among treatment parameters with regard to the quality properties. Duncan's multiple range test was also applied to determine the difference of means from the ANOVA, using a significance test level of ($p<0.05$).

RESULTS AND DISCUSSION

Quality of blueberry syrup with different heating times

The apparent viscosity as a function of the shear rate of the blueberry syrups with different mixing ratios of MTS and Xan (4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) after heating for 20 to 80 min at 90°C was investigated at 25°C (Figure 1). The viscosity values of the syrups increased significantly ($p<0.05$) with increasing Xan content at the same shear rate, and values were higher than those of the syrup without Xan (MTS/Xan = 4.0/0.0). The syrup without Xan had a lower viscosity value with longer heating time. All syrups with and without Xan exhibited shear thinning fluid properties, as the apparent viscosity decreased with increasing shear rate.

The condition of heating at 90°C for 40 min was selected for further investigation of the effect of Xan on syrup quality due to its similarity to the conditions of the hot-fill process used by food manufacturers. Data on the shear stress and shear rate of syrups (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) were plotted to describe the behavior of non-Newtonian fluids using the Herschel-Bulkley, power law and Bingham models (data not shown). Coefficients of determination (r^2) indicated that the power law equation (r^2 = 0.996-0.999) provided the best model of the experimental data (Steffe, 1996). Subsequently, the power law model was used to calculate the power law parameters, as shown in Equation (1):

$$\tau = K\dot{\gamma}^{n} \quad (1)$$

where τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), K = consistency coefficient ($Pa.s^n$), and n = flow behavior index.

For all syrup formulations with different mixing ratios of MTS and Xan, the consistency coefficient value (K) of syrup thickened by only MTS (15.6 $Pa.s^n$) was lower than the syrups containing Xan (25-52 $Pa.s^n$) (Table 1) and increased with Xan substitution. The flow behavior index (n) of all syrups was below 1, as expected for shear thinning liquids (Steffe, 1996). The substitution of Xan for MTS in the syrups also altered the flow behavior index (n) of the syrups from 0.7 to 0.61, 0.54 and 0.48 for 0.1, 0.2 and 0.3% Xan subsitution (Table 1), respectively. The n values decreased with increasing Xan substitution. The results suggested that the syrups containing Xan enhanced the viscosity of the products and exhibited more pronounced non-Newtonian behavior due to the flow behavior index deviating from the n value of 1 for a Newtonian fluid.

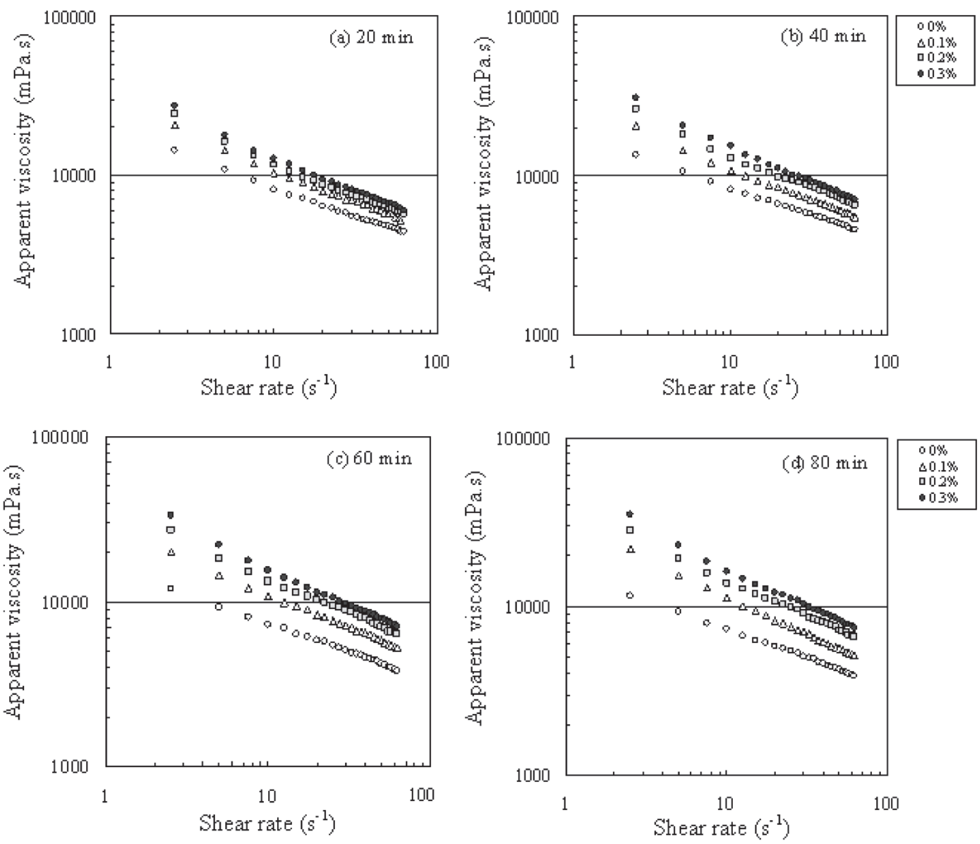

Figure 1 Apparent viscosity of blueberry syrups stabilized by MTS and Xan mixtures with different mixing ratios prepared from heating at 90°C for (a) 20 min; (b) 40 min; (c) 60 min; and (d) 80 min. Measurements were performed at 25°C.

Total soluble solids (TSS), pH values and water activity of the syrups with and without Xan were not significantly ($p>0.05$) different. The TSS and pH values of syrups were about 55.6-56.0° Brix and 2.45-2.48, respectively, whereas the water activity of all syrups was about 0.92.

The quality of the syrups was assessed by sensory evaluation using a 9-point hedonic scale. The results showed that the overall liking scores of the blueberry syrup containing 0.2%Xan were the highest among samples in terms of thickness and overall liking ($p<0.05$, Table 2). Therefore, the blueberry syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) was selected for storage studies and compared to syrup without Xan (4%MTS) as a control sample.

Quality change of blueberry syrup during storage

Batches (20 kg) of blueberry syrup containing 4% MTS and 4% MTS/Xan (mixing ratio = 3.8/0.2) were prepared for the storage stability test. The syrups with and without Xan were heated to 90°C, with further heating for 40 min, before being hot filled into OPA bags (500 g), hermetically sealed and cooled, and then kept at ambient temperature (average temperature 30±3°C). The product samples were tested for viscosity and other quality measurements over a 16-week storage period. The viscosity at shear rate 10 s^{-1} of blueberry syrups with and without Xan decreased with storage time (Figure 2). The rate of viscosity reduction of syrup containing 0.2% Xan was lower than that of syrup without Xan addition, as shown by the slope values of both syrups with and without Xan of about 19 and 41 mPa.s/d, respectively. The results indicated that Xan addition enhanced the viscosity stability of the syrup during storage at ambient temperature. The changes in the syrup viscosity during storage (Figure 2) were found to follow zero-order kinetics at ambient temperature (30±3°C) with $r^2 > 0.98$. Therefore, for both syrups, the viscosity (mPa.s) at a shear rate of 10 s ^{1}, as a function of storage time could be determined using Equations (2) and (3):

Table 1 Power law constants (K = consistency coefficient, n = flow behavior index) of syrups with and without Xan determined from the shear rate range of 2.5-62.5 s^{-1} at 25°C prepared from further heating for 40 min at 90°C.

Xan substitution (%)	K ($Pa.s^n$)	n (-)	r^2
0	15.9±0.1d	0.695±0.001a	0.996
0.1	25.6±0.5c	0.607±0.001b	0.999
0.2	36.7±0.2b	0.545±0.000c	0.999
0.3	52.3±0.3a	0.481±0.001d	0.996

Mean ± standard deviation values followed by different lower case letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

Table 2 Mean sensory scores of blueberry syrups with and without Xan prepared from heating 40 min at 90°C.

Xan substitution (%)	Appearance	Color	Odor	Thickness	Overall liking
0.0	6.6±0.7a	6.5±0.8a	6.2±1.0a	6.5±1.0b	6.1±1.0c
0.1	6.6±0.7a	6.4±0.7a	6.0±1.0a	6.8±1.1ab	6.6±0.9b
0.2	6.7±0.7a	6.5±0.7a	6.2±0.7a	7.4±0.6a	7.1±0.9a
0.3	5.5±0.9b	6.3±0.6a	5.9±1.0a	5.8±1.4c	5.9±0.9c

Mean ± standard deviation values followed by different lower case letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

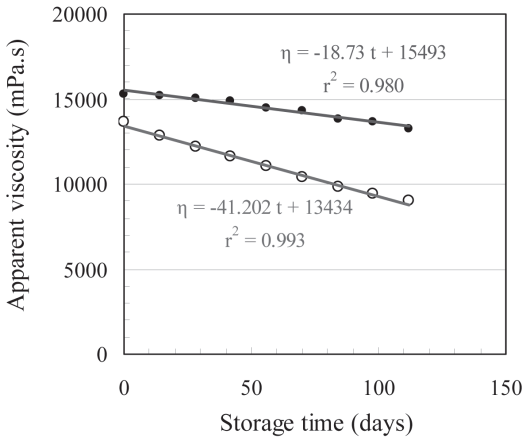

Figure 2 Apparent viscosity at shear rate 10 s^{-1} of blueberry syrups thickened by a combination of 4% MTS (○) and 4% MTS/Xan (3.8/0.2) (●) and heated for 40 min at 90°C during 16 wk storage at ambient temperature.

For syrup with 4% MTS;

$$\eta = -18.73\ t + 15493 \qquad (2)$$

For syrup with 4% MTS/Xan;

$$\eta = -41.202t + 13434 \qquad (3)$$

where: η = apparent viscosity (mPa.s) and t = storage time (d).

The shelf life can be defined as the length of time that a product may be stored under specified conditions without becoming unsuitable for use or consumption. Thus, for syrup, viscosity plays an important role in determining the end-of-shelf-life quality of the product. Using Equations (2) and (3), it was possible to estimate the shelf life of blueberry syrup kept at ambient temperature, if the criteria specifying the end of the shelf life are provided. For example, if the viscosity of syrup below 9,000 mPa.s is used as the end point of acceptable quality, the shelf life values of syrups with and without Xan were 346 and 107 d based on Equations (2) and (3), respectively. The results suggested that the addition of 0.2% Xan in the blueberry syrup could enhance the shelf life of the product in terms of viscosity.

Shear stress and shear rate data of fresh and stored blueberry syrups containing 4% MTS and 4% MTS/Xan were predicted using a power law model with the values of the coefficient of determination (r^2) about 0.997-0.999 (Table 3). The consistency coefficient value (K) of stored syrup thickened by MTS only (12 Pa.s^n) was significantly ($p<0.05$) lower than that of fresh samples (17 Pa.s^n) during storage, due to the degradation or hydrolysis of MTS with the low pH in the system. However, the addition of Xan in the syrup produced no significant ($p>0.05$) difference (Table 3) in the K values for fresh (33 Pa.s^n) and stored (32 Pa.s^n) products. The flow behavior index (n) of the syrups without Xan altered the n value of fresh sample from 0.591 to 0.622 (Table 3) after storage for 16 wk, whereas the n value of syrup containing 0.2% Xan changed from 0.514 to 0.496 with no significant ($p>0.05$) difference (Table 3). The difference in the power law constants of syrups with and without 0.2%Xan in Tables 3 and 1 was considered to be an effect of the production scale.

The TSS and pH values of both syrup formulations were about 55.4-56.0 °Brix and 2.42-2.48, respectively, over 16 wk of storage and showed no significant ($p>0.05$) differences. In the present study, the syrup was prepared as hot-filled product, with the addition of 1,000 mg/kg sorbic acid as an antimicrobial agent. Total plate count (TPC) and yeast/mold counts of syrups with and without Xan sampled before and after storage (16 wk) were found to be < 10 cfu/g.

The sensory evaluation of fresh blueberry syrups containing 0.2% Xan (MTS/Xan = 3.8/0.2) before storage exhibited a higher overall liking score than syrup without Xan addition (Table 4). After storage for 16 wk, there was no significant ($p>0.05$) difference in overall liking of the syrup with 0.2% Xan (MTS/Xan = 3.8/0.2) between the fresh and stored samples. The results suggested

Table 3 Power law constants of blueberry syrups with and without Xan packed in OPA film for 0 and 16 wk of storage.

Xan substitution (%)	Storage (wk)	K (Pa.s^n)	n (-)	r^2
0	0	17.1±1.4b	0.591±0.028b	0.998
0	16	12.1±0.3c	0.622±0.006a	0.999
0.2	0	33.2±0.2a	0.514±0.001c	0.999
0.2	16	31.9±0.3a	0.496±0.003c	0.997

Mean ± standard deviation values followed by different lower case letters within the same column are significanty (p<0.05) different by Duncan's multiple range test.

Table 4 Mean sensory scores of blueberry syrups with and without Xan packed in OPA film for 0 and 16 wk of storage.

Xan substitution (%)	Storage (wk)	Appearance	Color	Odor	Thickness	Overall liking
0	0	7.0±0.65b	6.8±0.62a	6.7±0.74a	7.0±0.47bc	7.0±0.59b
0	16	6.7±0.52c	6.5±0.57a	6.6±0.67a	6.7±0.81d	6.7±0.55c
0.2	0	7.5±0.57a	6.8±0.55a	6.7±0.48a	7.4±0.50a	7.6±0.50a
0.2	16	7.3±0.59a	6.7±0.48a	6.6±0.50a	7.3±0.44ab	7.4±0.50a

Mean ± standard deviation values followed by different lower case letters within the same column are significantly (p<0.05) different by Duncan's multiple range test.

that blueberry syrup obtained from a combination of 3.8%MTS and 0.2%Xan was more stable than syrups without Xan, in terms of viscosity and overall liking after storage for 16 wk.

CONCLUSION

The apparent viscosities of the blueberry syrups containing Xan were higher than those without Xan (MTS/Xan = 4/0) for all heating times at 90°C, whereas the TSS, pH and water activity values of syrups were not significantly (p>0.05) different among all samples. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) prepared by heating at 90°C for 40 min produced the highest overall liking score. The viscosity of syrups with and without 0.2%Xan decreased with storage time and followed zero-order kinetics. A lower rate of viscosity reduction was found in the syrup containing 0.2%Xan. Overall liking scores of the syrup with 0.2% Xan for both fresh and stored samples were not significantly (p>0.05) different and exhibited higher values than those without Xan. Therefore, Xan could be used in the food industry in fruit syrup to enhance the quality and stability during heating and storage.

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