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Effect of cross-linking on physicochemical properties of tapioca starch and its application in soup product

Rungtiwa Wongsagonsup[a], Thamonwan Pujchakarn[a], Suparat Jitrakbumrung[a], Weerawut Chaiwat[b], Asira Fuongfuchat[c], Saiyavit Varavinit[d], Somsak Dangtip[e,f], Manop Suphantharika[d,*]

[a] Food Technology Program, Mahidol University, Kanchanaburi Campus, Kanchanaburi 71150, Thailand
[b] Environmental Engineering and Disasters Management Program, Mahidol University, Kanchanaburi Campus, Kanchanaburi 71150, Thailand
[c] National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA), Ministry of Science and Technology, Klong Luang, Pathum Thani 12120, Thailand
[d] Department of Biotechnology, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[e] Department of Physics and NANOTEC CoE at Mahidol University, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
[f] ThEP Center, CHE, Ministry of Education, Bangkok 10400, Thailand

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ABSTRACT

Physicochemical properties of cross-linked tapioca starch (CLTS) with different cross-linking levels and their application as a thickening agent in soups were studied. The CLTS was prepared by cross-linking native tapioca starch suspended in alkaline solution (41.67% (w/w), pH 11) using a mixture (99:1 (w/w) ratio) of sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) at different concentrations ranged from 0.25% to 6.0% (w/w of starch) at 45 °C for 3 h. Starch paste clarity decreased with increasing concentration of STMP/STPP mixture. Variations of swelling power, solubility, pasting, gelatinization, and rheological properties of the CLTS were found. Thermogravimetric analysis exhibited higher thermal stability for the CLTS granules compared to the native one. Among the samples, the CLTS prepared using 1.0% STMP/STPP (1.0%-CLTS) and soup containing the 1.0%-CLTS exhibited the strongest gel characteristic and the greatest shear resistant properties. The 1.0%-CLTS improved the textural properties and sensory quality of soups.

1. Introduction

Tapioca starch, obtained from cassava root processing, is one of the most important export goods of Thailand. Native tapioca starch forms a clear but stringy and cohesive paste with bland flavor when it is cooked. However, limitations in using the native starch in some industrial food applications, e.g., low heat and shear resistance, and thermal decomposition of native starch, are found. Cross-linking modification is a common method utilized in the food industry to solve such problems. The new covalent bonds by cross-linking reaction can stabilize and strengthen the starch granules. Thus, the cross-linked starch granules are less sensitive to processing conditions, e.g., high temperature, extended cooking time, low pH and high shear, than the native ones (BeMiller, 2007, chap. 6; Wurzburg, 1986). Cross-link bonds occur at random locations in the starch granules. It was reported that both amylopectin and amylose in starch granules can be cross-linked. However, the amylose molecules had less of a tendency to be cross-linked (Jane, Xu, Radosavljevic, & Seib, 1992; Kasemsuwan & Jane, 1994). Starch paste from cross-linked starch is highly viscous, heavy bodied, shorter textured, and less likely to break down during extended cooking, exposure to low pH conditions, or when subjected to severe agitation (BeMiller, 2007). It is thus suitable for canned foods and other food applications for thickening and stabilizing the food system, e.g. soups, gravies, sauces, baby foods, fruit filling, pudding, and deep fried foods (BeMiller, 2007; Rutenberg & Solarek, 1984; Singh, Kaur, & McCarthy, 2007).

Cross-linking reaction is generally carried out by treating starch granules with multifunctional reagents capable of forming either ether or ester inter-molecular linkages between hydroxyl groups on starch molecules (Rutenberg & Solarek, 1984; Wurzburg, 1986). Many cross-linking agents are allowed for food use such as sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), phosphoryl chloride ($POCl_3$), and a mixture of adipic acid and acetic anhydride. Among them, the STMP, which is one of the most important food additives with low toxicity, is an efficient

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[*] Corresponding author. Tel.: +66 2201 5314; fax: +66 2354 7160.
E-mail address: manop.sup@mahidol.ac.th (M. Suphantharika).

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cross-linking agent (Gui-Jie, Peng, Xiang-Sheng, Xing, & Tong, 2006). Distarch phosphates, one type of cross-linked starch, are mostly produced by reacting starch granules with either STMP or $POCl_3$ under alkaline conditions (Wurzburg, 1986). The level of substitution is limited to 0.04% phosphorus (P) content when using only STMP but when starch is reacted with a mixture of STMP and STPP, the permitted P level is ten times higher (0.4% P) (CFR, 2013). Lim and Seib (1993) studied the preparation of starch phosphates and found that a mixture of STMP and STPP gave better results than using STMP alone to prepare distarch phosphates (cross-linked starches). Cross-linking reaction alters not only structural and physicochemical properties but also the physiological properties of starch (Chung, Shin, & Lim, 2008; Koo, Lee, & Lee, 2010). The effect of cross-linking on the properties of starch depends on the botanical source of starch (Lim & Seib, 1993; Liu, Ramsden, & Corke, 1999; Reddy & Seib, 2000), concentration and type of cross-linking agents (Kaur, Singh, & Singh, 2006; Wongsagonsup, Shobsngob, Oonkhanond, & Varavinit, 2005; Yoneya, Ishibashi, Hironaka, & Yamamoto, 2003) as well as reaction conditions used (Jyothi, Moorthy, & Rajasekharan, 2006; Luo, Huang, Fu, Zhang, & Yu, 2009; Varavinit, Paisanjit, Tukomane, & Pukkahuta, 2007). Using cross-linked starch with a proper cross-linking level could provide granule swelling without disruption and consequently control the rheological properties of starch-containing food products. High degree of cross-linking is not always an answer for textural improvement of food products since it may hinder the starch granules to undergo adequate swelling and viscosity formation especially in the process with a limited amount of heat (Thomas & Atwell, 1999, chap. 4).

Up to now, no information exists regarding some properties (e.g. rheological properties and thermal decomposition) of cross-linked tapioca starch (CLTS) and quality of soups containing CLTS with various degree of cross-linking. Thus, the objectives of this work were to investigate the physicochemical properties of CLTS prepared using different concentrations of the STMP/STPP mixture and to study quality of soups containing these CLTS samples.

2. Materials and methods

2.1. Materials

Tapioca starch was kindly provided by Siam Modified Starch Co. Ltd. (Pathum Thani, Thailand). Sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO). All other chemicals were of analytical grade.

2.2. Preparation of cross-linked tapioca starch

Cross-linked starch was prepared according to the method modified from Koo et al. (2010). Native tapioca starch (200 g) was dispersed in 280 mL of 0.1 N NaOH so as to obtain a solids concentration of 41.67% (w/w) and mixed with different concentrations (0.25, 0.5, 1.0, 1.5, 2.0, 4.0, and 6.0% (w/w) based on dry weight of starch) of a mixture of STMP/STPP (99:1 (w/w) ratio). The pH of suspension was about 11. The slurry was incubated at 45 °C for 3 h with stirring. The suspension was then neutralized to pH 6.5 with 0.1 N HCl, washed with distilled water for four times, and dried at 40 °C overnight. After that, the dried samples were then ground and sieved through a 100 mesh sifter.

2.3. Determination of phosphorus content and degree of substitution

Phosphorus content was determined by the method of AOAC (2006). The degree of substitution (DS) was calculated by using the equation described by Gui-Jie et al. (2006) as follows:

$$\mathrm{DS} = \frac{162P}{30.974(100 - 3.8734P)} \tag{1}$$

where P is the percentage of phosphorus content of cross-linked starch which was subtracted by that of the native one.

2.4. Determination of swelling power and solubility

Starch (0.5 g) was suspended in 15 mL distilled water and kept in a shaking water bath at a temperature of 85 °C for 30 min. The suspensions were cooled to room temperature (25 °C) and then centrifuged at 2200 × g for 15 min to separate the swollen paste sediments and supernatant. The solubilized starch was determined by drying the supernatant at 110 °C, overnight. The weights of swollen starch sediments and solubilized starch in supernatant were measured and used in the calculations of swelling power and solubility of the starch, respectively as follows:

$$\text{Swelling power (g/g)} = \frac{\text{Wet weight of swollen starch sediments}}{\text{Dry weight of starch} \times (100 - \%\,\text{solubility})} \tag{2}$$

$$\text{Solubility (\%)} = \frac{\text{Dry weight of solubilized starch} \times 100}{\text{Dry weight of starch}} \tag{3}$$

2.5. Determination of starch paste clarity

Clarity of starch paste was determined by measuring light transmittance according to the method of Craig, Maningat, Seib, and Hoseney (1989) with some modifications. Starch paste (1% (w/w)) was prepared by dispersing 0.25 g starch (db) in 25 g distilled water in a 50-mL centrifuge tube and then placed in a boiling water bath for 30 min with mild stirring. After cooling the starch paste solution to room temperature for 10 min, the percentage of light transmittance (%T) was read at 650 nm against distilled water using a double-beam UV–vis spectrophotometer (UV 1800, Shimadzu Corporation, Kyoto, Japan).

2.6. Thermogravimetry analysis

Thermogravimetry analysis was performed using a thermogravimetric analyzer (TGA) (Mettler-Toledo AG, Schwerzenbach, Switzerland). Starch powder was heated from 25 °C to 900 °C at a heating rate of 10 °C/min in a nitrogen stream. Adapted from Lii, Liao, Stobinski, and Tomasik (2002a, 2002b), percent weight loss was calculated by the percent weight difference between 250 °C and 320 °C.

2.7. Differential scanning calorimetry

The gelatinization temperatures and the enthalpy change (ΔH) of gelatinization of starch were determined using a differential scanning calorimeter (DSC) (DSC-1 STAR^e System, Mettler-Toledo AG, Schwerzenbach, Switzerland). Sample was mixed with distilled water at a ratio of 1:3 (w/w). The suspension (about 12 mg) was transferred to an aluminum pan and sealed hermetically. The sealed pan was then equilibrated at room temperature for 1 h. The sample was heated from 25 °C to 100 °C at a heating rate of 10 °C/min. A sealed empty pan was used as a reference.

Table 1
Physicochemical characteristics of native (NTS) and cross-linked tapioca starches (CLTS) prepared using different STMP/STPP concentrations.

Sample	P content (%)	DS ($\times 10^{-4}$)	Swelling power (g/g)	Solubility (%)	Light transmittance (%)	TG weight loss (%)
NTS	0.007 ± 0.001^{g}	0.00 ± 0.00^{g}	7.70 ± 0.15^{c}	3.33 ± 0.60^{bc}	35.65 ± 0.15^{a}	77.94
0.25%-CLTS	0.010 ± 0.001^{f}	1.18 ± 0.31^{f}	7.75 ± 0.25^{bc}	3.34 ± 0.57^{bc}	21.23 ± 1.82^{b}	77.50
0.5%-CLTS	0.014 ± 0.000^{e}	3.57 ± 0.08^{e}	8.23 ± 0.13^{ab}	4.43 ± 1.34^{ab}	15.97 ± 0.15^{c}	77.76
1.0%-CLTS	0.024 ± 0.001^{d}	9.03 ± 0.24^{d}	8.59 ± 0.17^{a}	5.81 ± 1.37^{a}	11.17 ± 0.15^{d}	76.58
1.5%-CLTS	0.025 ± 0.000^{d}	9.41 ± 0.16^{d}	7.54 ± 0.02^{c}	3.28 ± 1.20^{bc}	7.63 ± 0.29^{e}	76.06
2.0%-CLTS	0.029 ± 0.000^{c}	11.32 ± 0.16^{c}	7.45 ± 0.05^{c}	3.06 ± 0.19^{bc}	5.97 ± 0.21^{f}	76.42
4.0%-CLTS	0.031 ± 0.001^{b}	12.33 ± 0.48^{b}	6.44 ± 0.72^{d}	2.64 ± 1.04^{bc}	2.73 ± 0.15^{g}	75.75
6.0%-CLTS	0.033 ± 0.001^{a}	13.37 ± 0.32^{a}	6.31 ± 0.17^{d}	2.32 ± 0.21^{c}	1.90 ± 0.00^{h}	75.20

TG weight loss is the weight loss in the temperature range from 250 °C to 320 °C. Values with different superscripts within the same column are significantly different ($P < 0.05$). The percentage present in the sample code indicates the concentration of STMP/STPP mixture.

2.8. *Determination of pasting properties*

The pasting characteristics of starch were measured by a Rapid Visco-Analyzer (RVA) (Model-4, Newport Scientific Pty. Ltd., Warriewood, Australia) using standard 2 profile. Starch (1.5 g, db) and 25 g of distilled water (5.7% (w/w) starch solids content) were combined and stirred in an aluminum canister for 20–30 s before inserting the canister into the instrument. The viscosity was expressed in Rapid Visco Unit (RVU).

2.9. *Observation of starch morphology*

Morphology of the starch pastes obtained from the RVA were observed using a light and polarized light microscope (Olympus BX51, Olympus Optical Co. Ltd., Tokyo, Japan). The samples were diluted with 50% (w/w) glycerol before microscopic observation at 400× magnification.

2.10. *Rheological analysis*

Dynamic viscoelastic and steady flow properties of the starch pastes obtained from the RVA were determined at 25 °C using a rotational rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany) equipped with a cone and plate geometry (1° cone angle, 50 mm diameter, and 0.05 mm gap). For dynamic viscoelastic test, the frequency sweep was conducted by applying a controlled strain of 0.5% which was within the linear viscoelastic region (LVR), over a frequency range of 0.1–100 rad s^{-1} (Banchathanakit & Suphantharika, 2009). The degree of frequency dependence of the storage modulus (G') was determined by power law parameters as:

$$G' = A\omega^{B} \tag{4}$$

where G' is the storage modulus (Pa), ω is the oscillation frequency (rad s^{-1}), and A and B are the constants (Khondkar, Tester, Hudson, Karkalas, & Morrow, 2007; Yoneya et al., 2003).

After dynamic oscillatory test was completed, the sample was immediately subjected to steady flow test. The cone was programmed to ramp up and then down within a shear rates range of 1–300 s^{-1} in 6 min. The data of shear stress versus shear rate of shear ramping up and down was used to characterize flow behavior of the sample by fitting to the power law model as follows:

$$\sigma = K\dot{\gamma}^{n} \tag{5}$$

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

2.11. *Soup preparation and evaluation*

Soup formulation was adapted from the preparation method of Ravindran and Matia-Merino (2009). The standard recipe consisted of 2.3% corn starch, 19% fresh milk, 2% butter, 2% vinegar, 2% sugar, 1% bouillon cube, 1% salt, 0.5% pepper, and 70.2% water. Corn starch in the standard cream soup formulation was entirely replaced with cross-linked starches with various degree of cross-linking. The freshly prepared soup with a temperature of 60 °C was subjected for sensory evaluation by 30 untrained panelists. Attributes of flavor, viscosity, smoothness, and overall liking were evaluated using 9-point hedonic scaling test; the panelists scored on a scale of 1 (dislike extremely) to 9 (like extremely). The soup was cooled to room temperature prior to subjecting to rheological measurements using the method described earlier.

2.12. *Statistical analysis*

Data were analyzed using analysis of variance (ANOVA). Significant differences among means ($P < 0.05$) were analyzed by Duncan's multiple range test using the SPSS statistical software version 14.0 (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. *Phosphorus content and degree of substitution*

Native tapioca starch (NTS) contained 0.007% endogenous phosphorus content. The phosphorus (P) content of the cross-linked tapioca starch (CLTS) increased with increasing STMP/STPP concentration (Table 1). Lim, Kasemsuwan, and Jane (1994) reported that tapioca starch contained 0.008% organic P content, which was exclusively phosphate monoester. The maximum level of 0.4% P in modified starch using a combination of STMP and STPP is specified by regulation (CFR, 2013). Using up to 6.0% STMP/STPP mixture, the produced CLTS (6.0%-CLTS) contained 0.033% P which is under the regulation limit. By subtracting endogenous P in the NTS, the resulted P in the CLTS was calculated for degree of substitution (DS). With increasing the concentration of STMP/STPP mixture, the DS increased up to 13.37×10^{-4} for the 6.0%-CLTS.

3.2. *Swelling power and solubility*

With increasing concentration of STMP/STPP mixture up to 1.0%, the swelling power (SP) and solubility (SL) of the obtained CLTS significantly increased and were higher than those of the NTS. Thereafter, both values became lower than those of the NTS and decreased with further increase in STMP/STPP concentration from 1.5% to 6.0% STMP/STPP (Table 1). The microscopic observation (Fig. 1) shows that the slightly cross-linked starches retained their granule integrity and could absorb more water during heating, resulting in the increment of SP. With increasing cross-linking level, the granular structure of the CLTS was much stronger and consequently exhibited limited swollen granules. The explanation for these observations was that at low cross-linking levels, the repulsion between the adjacent starch molecules caused by the

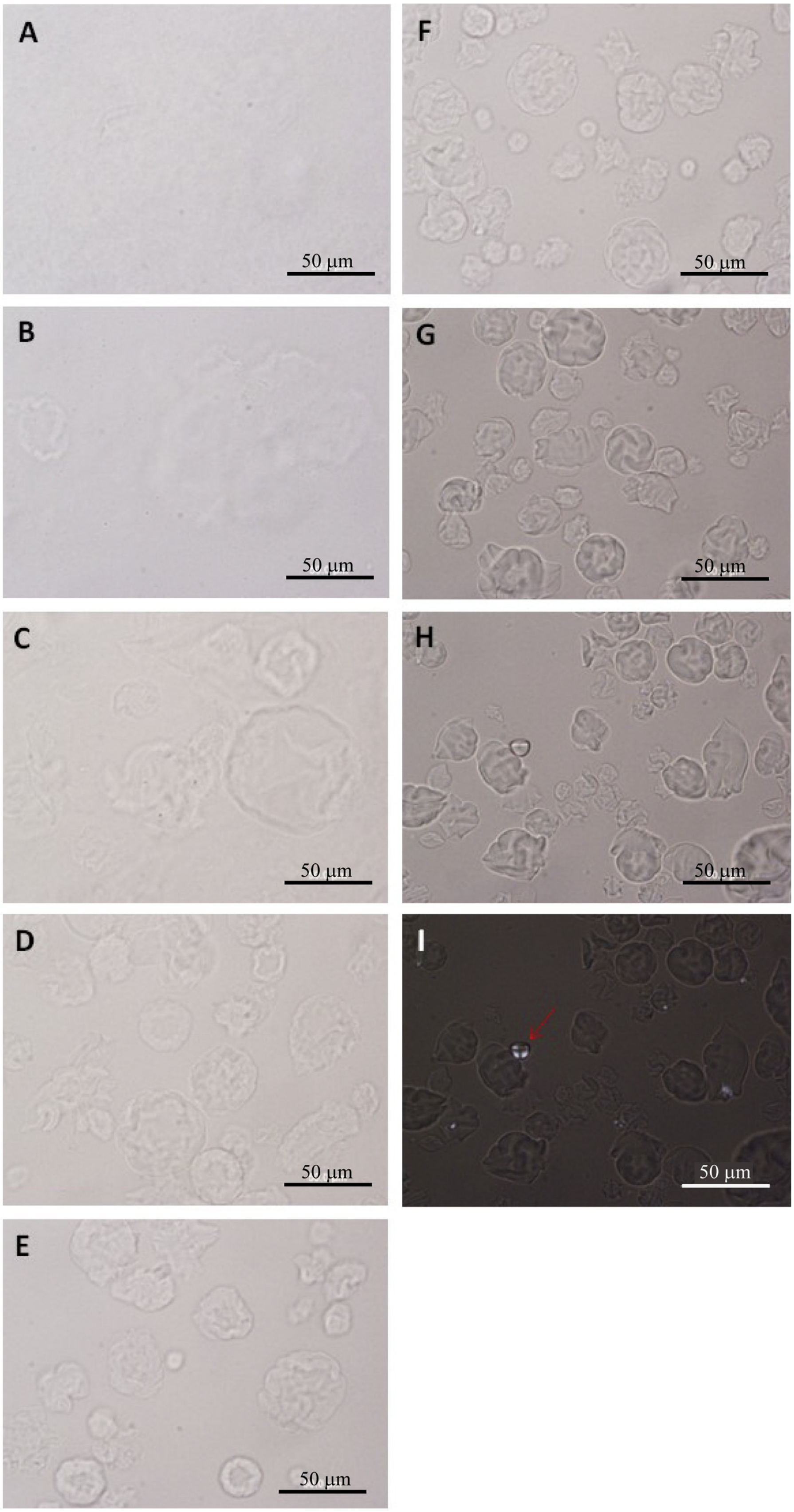

Fig. 1. Morphological properties of native (NTS) and cross-linked tapioca starch (CLTS) pastes prepared using different STMP/STPP concentrations observed under the light microscope (A–H) and the polarized light microscope (I): (A) NTS; (B) 0.25%-CLTS; (C) 0.5%-CLTS; (D) 1.0%-CLTS; (E) 1.5%-CLTS; (F) 2.0%-CLTS; (G) 4.0%-CLTS; (H) 6.0%-CLTS; and (I) 6.0%-CLTS. Slanted arrow indicates the intact granule with Maltese cross.

negatively charged phosphate groups of the cross-linked bridge might enhance the level of hydrated swollen starch granules, which resulted in increased SP (Kaur et al., 2006; Lim & Seib, 1993; Yoneya et al., 2003). In contrast, the decrease in the SP of the CLTS with increasing reagent concentration was due to the presence of more cross-links, which gave the constraints on the swelling behavior (Kaur et al., 2006; Yoneya et al., 2003). It has been reported that the higher concentrations of highly reactive cross-linking agents, e.g. $POCl_3$, which reacted predominately at the granule surfaces caused the formation of a hard crust that might restrict granule swelling (Huber & BeMiller, 2001).

The SL of the CLTS samples exhibited the same trend with their SP results. In general, it is known that the SL of cross-linked starches is mainly associated with their SP behavior (Kaur et al., 2006; Koo et al., 2010; Kurakake, Akiyama, Hagiwara, & Komaki, 2009; Liu et al., 1999). The higher the SP, the higher the SL is. At low levels of cross-linking, the penetration of water molecules into the granules was enhanced which would facilitate leaching of starch molecules into the aqueous phase, resulting in increased SL. In contrast, at higher cross-linking levels, the SP decreased due to the excessive cross-linking that might hinder the leaching of starch molecules from the starch granules and thus decreased SL.

3.3. Paste clarity

The NTS paste exhibited the highest light transmittance (35.65%) among all the starches tested (Table 1). Light transmittance of the CLTS pastes decreased with increasing STMP/STPP concentration. Especially, the 4.0%- and 6.0%-CLTS pastes exhibited a substantial decrease in paste clarity to 2.73 and 1.90% light transmittance, respectively. After gelatinization, the native starch granules were mostly disintegrated but the cross-linked starches exhibited more dense swollen granules especially at high concentrations of the cross-linking agents, which refracted rather than transmitted light, resulting in reduced paste clarity (Jyothi et al., 2006; Kaur et al., 2006; Koo et al., 2010; Reddy & Seib, 2000). These results were confirmed by the microscopic observation (Fig. 1) which will be discussed later. Determination of light transmittance of the thin pastes of cross-linked starches appears to be an alternative and more rapid method to determine the extent of cross-linking than the determination of shear stability of a hot starch paste using the amylograph (Lim & Seib, 1993).

3.4. Thermogravimetric analysis

Thermal degradation behavior of the NTS and CLTS samples by thermogravimetry (TG) is shown in Table 1. Thermogravimetric results showed that weight loss of the CLTS decreased with increasing STMP/STPP concentration from 77.94% for the NTS to 75.20% for the 6.0%-CLTS. This means that the CLTS granules exhibited more thermal stability and relatively stronger structure than the NTS. The results are consistent with those of Singh and Nath (2012), who reported that cross-linked sago starch had higher thermal stability than the native one, which makes it suitable for various industrial applications. Interestingly, the CLTS decomposed more quickly but the amount of remained part after decomposition was larger than that of the untreated starch (data not shown). The presence of bulky phosphate groups leading to an increase in amorphous region in the CLTS granules would facilitate thermal decomposition of the CLTS. This is in agreement with Singh and Nath (2012), who found that XRD spectra of cross-linked sago starch showed more amorphous region with reduced diffraction intensity, which might be due to the replacement of some hydroxyl groups with phosphate groups during cross-linking. In addition, the presence of larger amount of ash as phosphorus content in the CLTS compared to the NTS had negligible effect on the calculated weight loss by TGA. For example, in an extreme case, the difference in weight loss between the NTS and the 6.0%-CLTS was 2.74%, whereas the difference in the P content between these two starches was only 0.026% (Table 1). This means that the calculated weight loss by TGA could be reasonably used as a measurement for the thermal stability of the CLTS granules.

Table 2
Gelatinization properties of native (NTS) and cross-linked tapioca starches (CLTS) prepared using different STMP/STPP concentrations.

Sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
NTS	64.1 ± 0.0^{d}	69.9 ± 0.1^{ab}	79.5 ± 0.4^{a}	14.9 ± 0.5^{d}
0.25%-CLTS	64.7 ± 0.0^{ab}	69.2 ± 0.0^{cd}	78.9 ± 0.1^{bc}	15.8 ± 0.3^{cd}
0.5%-CLTS	64.7 ± 0.0^{ab}	69.0 ± 0.4^{d}	79.2 ± 0.2^{ab}	16.7 ± 0.5^{ab}
1.0%-CLTS	64.7 ± 0.0^{ab}	69.6 ± 0.0^{bc}	79.1 ± 0.3^{ab}	15.8 ± 0.1^{cd}
1.5%-CLTS	64.3 ± 0.3^{cd}	69.5 ± 0.6^{bcd}	78.8 ± 0.1^{bc}	15.0 ± 0.2^{d}
2.0%-CLTS	64.6 ± 0.2^{bc}	69.5 ± 0.4^{bcd}	78.7 ± 0.0^{bc}	15.0 ± 0.0^{d}
4.0%-CLTS	65.0 ± 0.1^{a}	69.8 ± 0.2^{ab}	78.9 ± 0.2^{bc}	16.0 ± 0.4^{bc}
6.0%-CLTS	64.9 ± 0.3^{ab}	70.3 ± 0.2^{a}	78.4 ± 0.3^{c}	17.5 ± 0.4^{a}

T_o, T_p, and T_c are the onset, peak, and conclusion gelatinization temperatures, respectively. ΔH is the gelatinization enthalpy. Values with different superscripts within the same column are significantly different ($P < 0.05$). The percentage present in the sample code indicates the concentration of STMP/STPP mixture.

3.5. Gelatinization properties

The onset (T_o), peak (T_p), and conclusion (T_c) gelatinization temperatures and the gelatinization enthalpy (ΔH) of the NTS and CLTS prepared using different STMP/STPP concentrations are shown in Table 2. In general, the magnitudes of T_o and ΔH slightly increased with increasing concentration of the cross-linking agent compared to those of the NTS. The results confirmed that the formation of additional cross-linked covalent bonds tightened the molecular organization of starch molecules and thus reinforced the integrity of starch granules. Therefore, the CLTS gelatinized at a higher temperature and more heat was required for gelatinization than its native counterpart (Rutenberg & Solarek, 1984). The ΔH primarily reflects the loss of molecular (double-helical) order rather than crystalline order within the starch granules (Cooke & Gidley, 1992). It refers to the energy required to disrupt the starch granule structure (Liu et al., 1999). Therefore, higher ΔH values indicate higher granule stability. However, the T_c value slightly decreased with increasing cross-linking level, whereas the T_p value seemed to be unaffected by cross-linking. It was reported that the gelatinization temperature of starch was not affected by cross-linking while the ΔH increased with increasing cross-linking level (Choi & Kerr, 2004; Yeh & Yeh, 1993). Therefore, the impact of cross-linking on gelatinization properties depended on the level of cross-linking.

3.6. Pasting properties

Considering that cross-linked starch is stable during pasting at high temperature with shearing, the RVA standard 2 profile was chosen on the basis that it has a longer holding time at 95 °C of 5 min and a longer total test time of 23 min compared to 2.5 min and 13 min, respectively for the standard 1 profile. Typically for native starch and flour, a proposed standard RVA procedure is holding at 95 °C for 4 min with a total test time of 16 min (Batey & Curtin, 2000). The most significant effect of these different holding times is on the holding strength (trough viscosity) and consequently breakdown and setback which are derived from the trough value. Lower values were obtained for the trough with longer holding times at 95 °C (Batey & Curtin, 2000).

The RVA pasting parameters of the NTS and CLTS samples are shown in Table 3. The pasting characteristics were governed by the level of cross-linking. Breakdown, i.e. the difference between

Table 3
Pasting properties of native (NTS) and cross-linked tapioca starches (CLTS) prepared using different STMP/STPP concentrations.

Sample	Peak viscosity (RVU)	Trough (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
NTS	165.5 ± 0.2^{b}	84.8 ± 0.8^{d}	80.7 ± 0.6^{a}	149.3 ± 0.1^{d}	64.5 ± 0.7^{c}	68.8 ± 4.0^{ab}
0.25%-CLTS	186.4 ± 2.2^{a}	119.2 ± 1.3^{c}	67.3 ± 1.0^{b}	183.7 ± 2.2^{c}	64.5 ± 0.9^{c}	69.3 ± 0.6^{ab}
0.5%-CLTS	184.5 ± 12.7^{a}	134.2 ± 8.7^{b}	50.4 ± 4.0^{c}	238.0 ± 8.7^{b}	103.8 ± 0.0^{b}	68.2 ± 0.9^{b}
1.0%-CLTS	159.3 ± 2.5^{b}	145.5 ± 2.7^{a}	13.8 ± 5.2^{d}	282.0 ± 3.9^{a}	136.5 ± 6.6^{a}	70.2 ± 0.9^{ab}
1.5%-CLTS	87.9 ± 0.5^{c}	87.4 ± 0.5^{d}	0.5 ± 0.1^{e}	141.1 ± 1.2^{d}	53.7 ± 0.8^{d}	72.7 ± 1.0^{a}
2.0%-CLTS	27.3 ± 2.0^{d}	27.2 ± 1.8^{e}	0.1 ± 0.2^{e}	50.3 ± 1.8^{e}	23.1 ± 0.0^{e}	69.8 ± 0.9^{ab}
4.0%-CLTS	5.0 ± 2.2^{e}	3.8 ± 2.1^{f}	1.3 ± 0.1^{e}	5.3 ± 1.8^{f}	1.5 ± 0.3^{f}	67.7 ± 0.5^{b}
6.0%-CLTS	3.0 ± 1.0^{e}	2.2 ± 0.4^{f}	0.8 ± 0.6^{e}	3.7 ± 0.5^{f}	1.5 ± 0.1^{f}	66.7 ± 1.0^{b}

Values with different superscripts within the same column are significantly different ($P < 0.05$). The percentage present in the sample code indicates the concentration of STMP/STPP mixture.

peak viscosity and holding strength, of all the CLTS decreased as the STMP/STPP concentration increased, indicating the improvement of heat and shear tolerance. The formation of covalent cross-links between starch chains strengthens the swollen granules against breakage under the conditions of high temperature and mechanical shear, which minimizes or prevents loss in viscosity (Jyothi et al., 2006; Wurzburg, 1986). Peak viscosity increased with STMP/STPP concentration up to 0.25%, while final viscosity and setback (final viscosity minus trough viscosity) increased with STMP/STPP concentration up 1.0%. After these particular STMP/STPP concentrations, those values declined with further increase in STMP/STPP concentration. At a low degree of cross-linking, i.e. for the 0.25–1.0%-CLTS, most of the starch granules swelled to a larger size and partially disintegrated, resulting in high values of peak and final viscosities. Because of the proper integrity of the 0.25–1.0%-CLTS granules, they can absorb more water leading to a larger size of the swollen granules which occupy more volume fraction in the system, consequently exhibit a higher viscosity development during cooling, resulting in a higher setback. It has been reported that cross-linking depressed the disintegration of starch granules which contributed to high peak viscosity and setback (Kurakake et al., 2009); and the persistence of the swollen granules after cooling resulted in higher final viscosity (Liu et al., 1999). Previous studies have shown that higher peak and cold paste viscosities of cross-linked waxy rice starch could be due to the degree of cross-linking was sufficient to prevent granule disruption but not great enough to restrict swelling (Liu et al., 1999). The 1.5%- and 2.0%-CLTS showed a continual and progressive increase in viscosity throughout the RVA pasting with non-detectable breakdown, due to the higher level of cross-linking and consequently a reduction of the granule swelling. With increasing the degree of cross-linking, the swelling of starch granules was depressed and resulted in a decrease in viscosity. It has been reported that the bonding between starch chains strengthened by cross-linking might increase the resistance of starch granules to swell, leading to lower peak viscosity (Jyothi et al., 2006; Liu et al., 1999). The 4.0%- and 6.0%-CLTS showed no pasting curve, indicating excessive cross-linking. Because of their severely limited swelling, the 4.0%- and 6.0%-CLTS were unsuitable for use as thickening agents in food products. They would be applied for increasing amount of resistant starch (RS type 4) in food products (Woo & Seib, 2002; Yeo & Seib, 2009).

3.7. Microscopic observation

The morphology of the NTS and CLTS granules present in the pastes obtained from the RVA is shown in Fig. 1. The NTS granules had completely disintegrated after gelatinization (Fig. 1A), whereas the CLTS granules remained almost intact (Fig. 1B–H). The integrity of the swollen CLTS granules increased with increasing STMP/STPP concentration, indicating their tolerance to the conditions of high temperature and shear. Due to the excessive cross-linking of the 6.0%-CLTS sample, Maltese cross of some intact granules was observed under the polarized light microscope (Fig. 1I).

3.8. Rheological properties of starch pastes

Since the 4.0%- and 6.0%-CLTS had no viscosity increment during pasting, they were not used for rheological study. Using a dynamic viscoelastic test, the information of gel structure can be acquired from its mechanical spectrum, i.e. variation of G' (storage modulus) and G'' (loss modulus) as a function of angular frequency. A solid-like behavior of all starch pastes obtained from the RVA was exhibited with $G' > G''$ along the measured frequency range (Fig. 2). The frequency dependence of G' and G'' of all samples was found and a higher frequency dependence of G'' of the 1.5%- and 2.0%-CLTS was present markedly. The magnitudes of G' and G'' of all CLTS pastes were higher than those of the NTS paste (Fig. 2A and B, respectively). There was no swollen granule found in the NTS paste, resulting in the inferior viscoelastic properties. It was reported that G'' and complex viscosity (η^*) of cross-linked waxy maize starch were higher than those of unmodified starch (Khondkar et al., 2007). For cross-linked starches, the overall elasticity of the suspensions is depressed when the particle rigidity decreases (Nayouf, Loisel, & Doublier, 2003). The lower deformability of the particles or the higher their granule rigidity, the higher G' is. The magnitudes of G' and G'' increased initially with increasing STMP/STPP concentration but then decreased at cross-linking agent concentrations of higher than 1.0%, which were in the same trend with the final viscosities from the RVA profiles (Table 3). The 1.0%-CLTS paste exhibited the highest G' and G'' values among the other CLTS and the native one, indicating that the volume fraction of swollen granules of the 1.0%-CLTS was high enough (confirmed by its highest SP value, Table 1) to produce both elastic network-like structure and friction between the granules. Moreover, a magnitude of loss tangent ($\tan\delta$), i.e. a value of G''/G', of the 1.0%-CLTS paste was low and almost stable as compared to those of the NTS and other CLTS samples (Fig. 2C), indicating higher gel strength and consistency. The NTS paste had higher $\tan\delta$ values than all the CLTS samples. Yoneya et al. (2003) also found that the $\tan\delta$ of unmodified starch was higher than that of cross-linked potato starch. In general, the increase of G' accompanied by a decrease of $\tan\delta$ suggests a formation of polymer cross-linking (Yoneya et al., 2003).

Power law constants (A and B) for a relationship between G' and frequency calculated using Eq. (4) are shown in Table 4. The coefficients of determination (R^2) reported in Table 4 showed high correlation ($R^2 \sim 0.976$–0.997) between G' and ω. It is well known that $B = 0$ for a covalent gel, while $B > 0$ for a physical gel. The B value is related to the strength of the gel (Hsu, Lu, & Huang, 2000). The 1.0%-CLTS paste had the lowest B value and the highest A value, indicating that it had a stronger gel structure compared to the other CLTS and NTS samples. The results are in agreement with those of Khondkar et al. (2007), who reported that the cross-linked waxy maize starch had lower B value and higher A value than the native

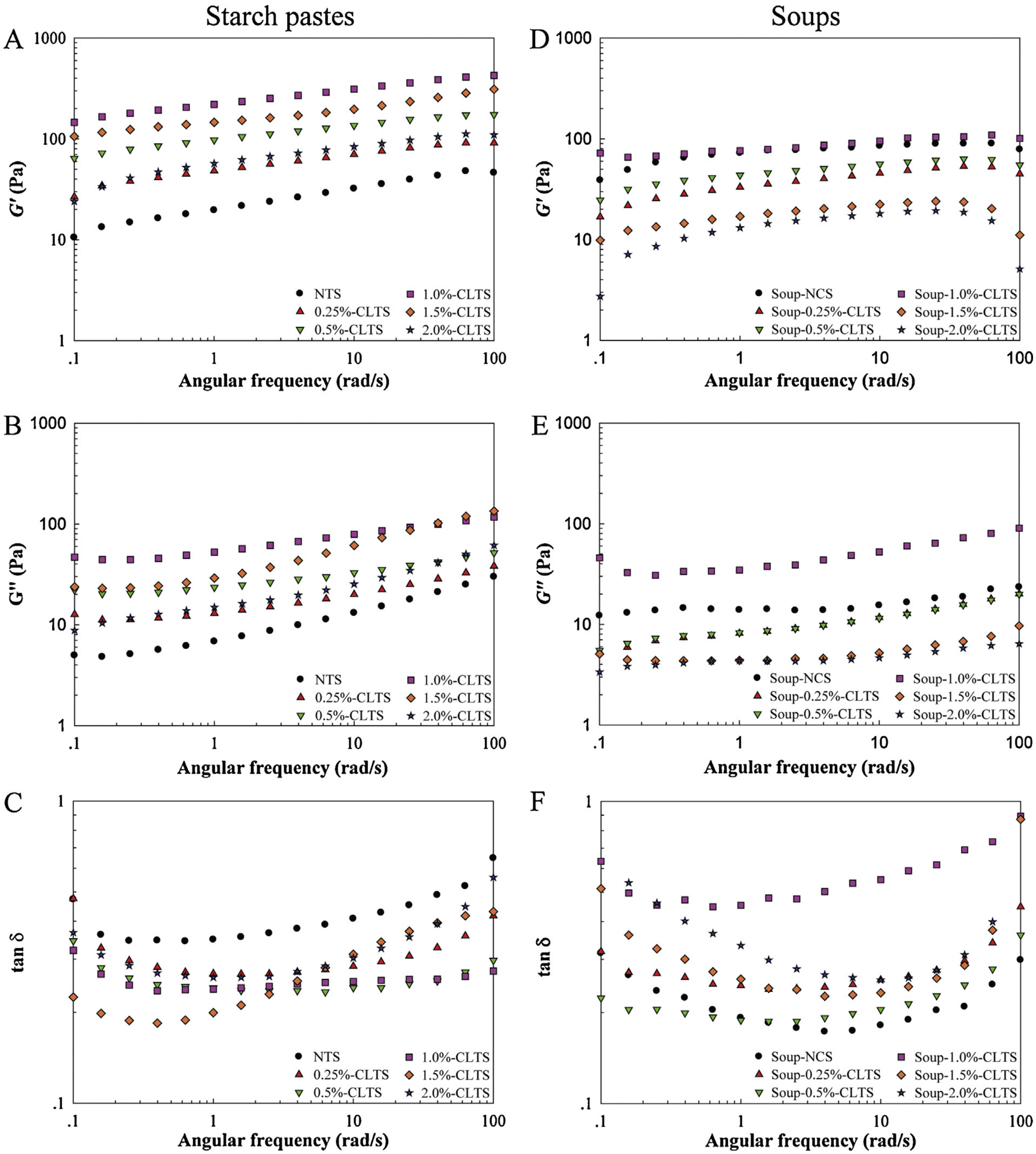

Fig. 2. Dynamic viscoelastic properties of 5.7% (w/w) native (NTS) and cross-linked tapioca starch (CLTS) pastes prepared using different STMP/STPP concentrations (A–C) and soups containing 2.3% (w/w) native corn starch (NCS) or CLTS with various degree of cross-linking (D–F). All measurements were performed at 0.5% strain and 25 °C.

one, indicating that the cross-linked starch gel was stronger than the native starch gel. It was also reported that cross-linked potato starches prepared using up to 500 ppm $POCl_3$ concentration also exhibited higher *A* value and lower *B* value compared to native potato starch (Yoneya et al., 2003).

For steady flow test, the NTS and 0.25%- and 0.5%-CLTS pastes displayed clockwise hysteresis loops of thixotropic behavior in the shear rate versus shear stress curves obtained in an increasing-order of shear (up curve) and a decreasing-order of shear (down curve) (Fig. 3A). Thixotropy appeared to be less pronounced for the 1.0%-, 1.5%-, and 2.0%-CLTS pastes. The 1.0%- and 1.5%-CLTS pastes exhibited similar combined hysteresis loops, i.e. anticlockwise loop (antithixotropic behavior) at low shear rates and clockwise loop at higher shear rates ($\dot{\gamma} > 50\,\mathrm{s}^{-1}$). The antithixotropic behavior would be ascribed to a rearrangement of closed-packed particles thus yielding a higher organization of the system (Barnes, Hutton, & Walters, 1989). However, there was almost no hysteresis loop present for the 2.0%-CLTS sample.

Power law constants (*K* and *n*) for a relationship between shear stress and shear rate calculated using Eq. (5) to characterize the flow behavior of the sample pastes are presented in Table 4. Both up curve and down curve data of all starch pastes were well fitted ($R^2 > 0.980$) to the power law model (Eq. (5)). All the starch pastes exhibited shear-thinning behavior ($n < 1$) of flow. The clockwise loops can be interpreted as structure breakdown by the applied shear to alter a structure or form a new structure, which

Table 4
Power law constants for relationship between storage modulus and frequency ($G' = A\omega^B$) and between shear stress and shear rate ($\sigma = K\dot{\gamma}^n$) of native (NTS) and cross-linked tapioca starch (CLTS) pastes (5.7% (w/w)) and soups containing 2.3% (w/w) native corn starch (NCS) or CLTS prepared using different STMP/STPP concentrations.

Sample	Dynamic viscoelastic test			Steady flow test					
	A (Pa s)	B (slope)	R^2	K (Pa s^n) (up)	n (−) (up)	R^2 (up)	K (Pa s^n) (down)	n (−) (down)	R^2 (down)
NTS	19.38	0.22	0.995	69.78	0.33	0.995	18.05	0.56	1.000
0.25%-CLTS	46.80	0.17	0.976	169.01	0.20	0.994	19.10	0.55	0.998
0.5%-CLTS	96.14	0.15	0.991	171.38	0.22	0.995	23.53	0.53	0.997
1.0%-CLTS	218.65	0.15	0.997	62.07	0.38	0.980	41.46	0.47	1.000
1.5%-CLTS	146.98	0.15	0.986	31.43	0.34	0.997	20.22	0.43	0.993
2.0%-CLTS	55.96	0.17	0.986	4.67	0.50	0.999	2.95	0.58	0.999
Soup-NCS	65.45	0.12	0.823	1.59	0.47	0.988	1.03	0.54	0.992
Soup-0.25%-CLTS	32.59	0.14	0.992	1.44	0.35	0.986	0.78	0.47	0.987
Soup-0.5%-CLTS	42.49	0.11	0.968	2.26	0.51	0.994	1.60	0.57	0.990
Soup-1.0%-CLTS	76.85	0.09	0.988	3.53	0.49	0.998	2.96	0.52	0.998
Soup-1.5%-CLTS	16.67	0.13	0.981	0.48	0.41	0.992	0.31	0.48	0.983
Soup-2.0%-CLTS	12.92	0.13	0.915	0.36	0.41	0.993	0.24	0.48	0.985

The percentage present in the sample code indicates the concentration of STMP/STPP mixture.

maintained a shear-thinning behavior on following shear ramping (Achayuthakan & Suphantharika, 2008). Therefore, a decrease in K values and increase in n values of the down curves was observed as compared to those of the up curves (Table 4). The rheological properties of starch pastes are mostly governed by the volume fraction of the swollen starch granules and their deformability (Da Silva, Oliveira, & Rao, 1997). The limited swollen granules of the 1.5%- and 2.0%-CLTS would provide low volume fraction in the system and have more available space among them, and thus less intergranular interaction, resulting in lower K values. Even though the NTS and 0.25%- and 0.5%-CLTS granules would provide more volume fraction but they could have high deformability, resulting in lower K values obtained from the down curves. The less difference in K and n values obtained from the up and down curves of the CLTS pastes prepared using 1.0%, 1.5%, and 2.0% cross-linking agents can be attributed to small changes in the structure of starch pastes on the applied shear, indicating that the structure of such pastes was strong and shear-resistant. The 1.0%-CLTS paste showed the least difference in K value obtained from the up curve and the down curve, i.e. 33% reduction from the up curve value. Therefore, the 1.0%-CLTS would be appropriate as a thickening agent used in food product because it could stabilize its viscosity via shearing.

3.9. *Rheological properties of soups*

The 0.25–2.0%-CLTS were tested as a thickening agent in soup product. Normal corn starch (NCS) was chosen as a control as it is typically used as a thickening agent in soup formulations (Ravindran & Matia-Merino, 2009). For dynamic viscoelastic properties, the prepared soups (Fig. 2D–F) showed a similar trend to those of the modified starch pastes (Fig. 2A–C). The experimental data were well fitted ($R^2 \sim 0.823$–0.992) to Eq. (4) to determine the A and B values (Table 4). Soup containing the 1.0%-CLTS (soup-1.0%-CLTS) provided the greatest A value and the lowest B value, indicating the highest gel rigidity among all the soups tested, which would be attributed to the large swelling volume and the rigidity of the swollen 1.0%-CLTS granules.

For steady flow test, all soups except for the soup-1.0%-CLTS exhibited time-dependent shear-thinning (thixotropic) behavior (Fig. 3B). The soup-1.0%-CLTS had combined hysteresis loops which is very similar to that of the 1.0%-CLTS paste, i.e. anticlockwise loop at low shear rates and clockwise loop at higher shear rates ($\dot{\gamma} > 50\,\text{s}^{-1}$). The up and down curves data of all soups were well fitted ($R^2 > 0.983$) to the power law model (Eq. (5)). The power law parameters (K and n) are presented in Table 4. Again the soup-1.0%-CLTS showed the highest K values for both up and down curves

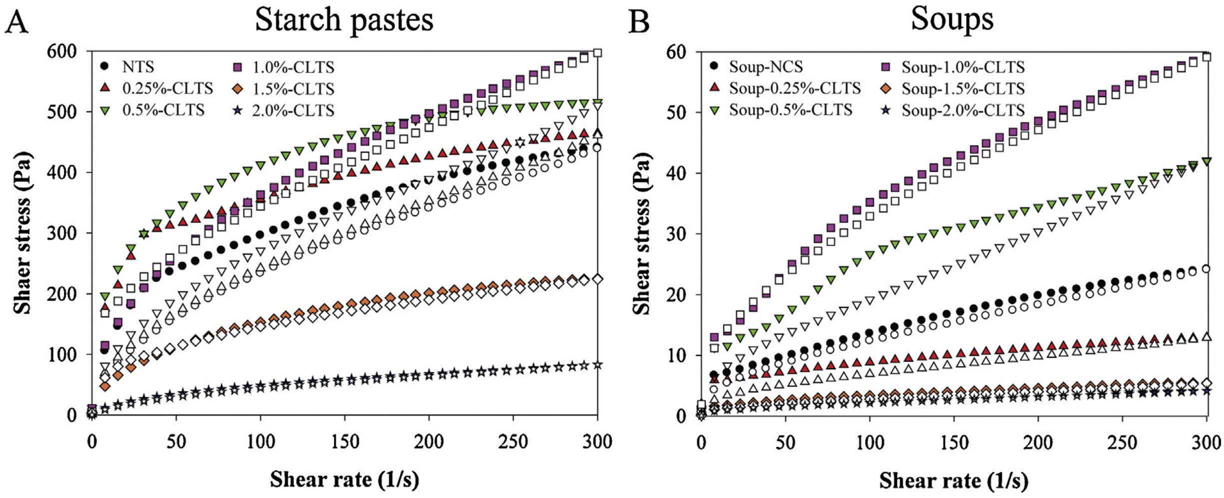

Fig. 3. Flow curves of 5.7% (w/w) native (NTS) and cross-linked tapioca starch (CLTS) pastes prepared using different STMP/STPP concentrations (A) and soups containing 2.3% (w/w) native corn starch (NCS) or CLTS with various degree of cross-linking (B). All measurements were performed at 25 °C. Closed symbols represent the ascending part and open symbols the descending part of the flow curves.

Table 5
Sensory evaluation of soups containing 2.3% (w/w) native corn starch (NCS) or cross-linked tapioca starch (CLTS) prepared using different STMP/STPP concentrations.

Sample	Flavor	Viscosity	Smoothness	Overall liking
Soup-NCS	6.33^{c}	6.53^{b}	6.80^{a}	6.68^{b}
Soup-0.25%-CLTS	6.20^{c}	6.38^{b}	6.80^{a}	6.55^{b}
Soup-0.5%-CLTS	6.98^{ab}	6.50^{b}	7.08^{a}	6.85^{b}
Soup-1.0%-CLTS	7.08^{a}	7.50^{a}	7.45^{a}	7.43^{a}
Soup-1.5%-CLTS	6.00^{c}	4.58^{c}	5.73^{b}	5.70^{c}
Soup-2.0%-CLTS	6.43^{bc}	5.05^{c}	5.83^{b}	5.88^{c}

Values with different superscripts within the same column are significantly different ($P < 0.05$). The percentage present in the sample code indicates the concentration of STMP/STPP mixture.

ramping and exhibited the least difference in K values from the up curve and the down curve, i.e. 16% reduction from the up curve value. In terms of these rheological properties, the soup-1.0%-CLTS had the greatest consistency and was highly shear-resistant. The results are consistent with the rheological behaviors of the starch pastes. Therefore, the 1.0%-CLTS provided the great consistency improvement of the soups.

3.10. Sensory quality of soups

Sensory evaluation of soups was performed using the 9-point hedonic scaling test. Typically, the hedonic scale is designed for use with untrained panelists who frequently use the product of interest, and it is considered the standard for assessing degree of liking. The panelists are urged to report responses on the basis of their own immediate feeling without exercising conscious effort to remember or to judge (Amerine, Pangborn, & Roessler, 1965, chap. 8).

Cream soups containing NCS (control) or CLTS with various degree of cross-linking were evaluated by a panel that scored their linking of flavor, viscosity, smoothness, and overall linking. Flavor is a complex perception of taste along with aroma, while viscosity and smoothness reflects the perception of consistency of soups. Table 5 shows the results as mean value of sensory score for the control soup and those containing CLTS. The mean scores of sensory evaluation showed that the soups containing NCS or 0.25%-, 0.5%-, and 1.0%-CLTS were within the acceptable range (6–7 on a scale of 1–9). However, the soups containing 1.5%- and 2.0%-CLTS had significantly ($P < 0.05$) lower perceived viscosity, smoothness, and overall liking compared to other samples. Statistical analysis shows that the soup containing 1.0%-CLTS received the highest sensory scores for flavor, textural attributes (viscosity and smoothness), and overall liking among all the soups tested. These data showed that sensory quality of the soup can be related to its rheological properties. The good rheological properties, i.e. a strong gel structure (high A value and low B value), high consistency, and high shear resistance of the 1.0%-CLTS had a positive effect on the overall sensory quality of soups. Consequently, the 1.0%-CLTS was a suitable thickening agent for the improvement of textural and sensory properties of the soup product.

4. Conclusions

The physicochemical properties of cross-linked tapioca starch and the quality of soups containing the cross-linked tapioca starch were determined by the degree of cross-linking. With a proper cross-linking level using 1.0% STMP/STPP concentration, the cross-linked tapioca starch, i.e. 1.0%-CLTS provided the highest viscosity with little granule disruption during pasting. Its paste also had satisfied rheological properties as exhibiting the strongest gel characteristic (the highest A value and the lowest B value) and the greatest shear resistant behavior (the smallest reduction of the K value during shear cycling). Soup containing the 1.0%-CLTS was also evaluated to have the best rheological and sensory properties. The 1.0%-CLTS could be suitably applied in soup product as a thickening agent for improvement of textural and sensory qualities.

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