Effect of galactomannan hydrocolloids on gelatinization and retrogradation of tapioca and corn starch

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original scientific paper

Summary

The aim of the present study was to investigate the effect of galactomannan hydrocolloids (guar gum and locust bean gum) on gelatinization and retrogradation of tapioca and corn starch. Differential scanning calorimetry (DSC) was used to characterize the behaviour of tapioca and corn starch with and without additives.
Results showed that guar gum and locust bean gum retarded the retrogradation of tapioca and corn starch at both investigated temperatures (4 and 25 °C). Guar gum retarded retrogradation of tapioca starch more than locust bean gum, on the other hand, locust bean gum had a greater effect on reduction of the recrystallization of corn starch. Temperatures of gelatinization did not vary significantly in starch-hydrocolloid systems. Additions of galactomannan hydrocolloids caused a decrease in gelatinization enthalpy of both starches.

Keywords: corn and tapioca starch, gelatinization, hydrocolloids, retrogradation

Introduction

In the food production, starch and hydrocolloids have a special importance and wide variety of applications. In general, they are used to provide control of moisture and water mobility, improve overall product quality and/or stability, reduce cost, and/or facilitate processing (Shi and BeMiller, 2002; Funami et al., 2005). Guar gum, locust bean gum, alginates, carrageenans and xanthan gum are among the hydrocolloids most frequently employed as stabilizers in food industry (Mali et al., 2003).
Starch functionality depends on the molecular structure of the amylose and amylopectin components and their interactions with their environment during two main processes, gelatinization and retrogradation (Lewen et al., 2003). One of the most important physical properties of starch is gelatinization, phase transition of starch granules from an ordered to a disordered state during heating with excess water. It induces number of changes in starch granules, such as swelling, exudation of amylose and amylopectin, granule disruption, lose of birefringence, and increased viscosity (Alavi, 2003; Karapantsios et al., 2002; Li et al., 2004). Structural and rheological characteristics can be altered by hydrocolloid addition. Starch's gelatinization temperature (onset, peak and conclusion temperature) is not modified by hydrocolloids (Biliaderis et al., 1997; Liu and Eskin, 1998; Rojas et al., 1999). However, swelling of granules can be affected by addition of hydrocolloids, suggesting that swelling is enhanced in their presence (Rojas et al., 1999; Teacante and Doublier, 1999).
Retrogradation of gelatinized starch occurs in many starch-food systems. Retrogradation of starch is a term used for the changes that occur in gelatinized starch from an initially amorphous or disordered state to a more ordered crystalline state and the tendency of starch pastes to thicken and to form stiff gels. Retrogradation rate is affected by the ratio of amylose and amylopectin, molecular size, temperature, pH, lipids, hydrocolloids, sugar and botanical sources (Aee et al., 1998). Ahmad and Williams (2001) reported that the addition of galacomannans significantly improved the freeze-thaw stability of sago starch gels. Liu and Thompson (1998) studied the effect of moisture content on retrogradation of waxy corn starches. They found that the effect of moisture content on retrogradation depends on the molecular structure of starches. Moisture content and initial heating temperature in gelatinization had different influence on retrogradation of the four types of waxy corn starches. Jouppila and Roos (1997) proposed that melting temperatures (onset, peak and conclusion temperature) of crystallized starch increases with increasing storage temperature.
Differential scanning calorimetry (DSC) is a thermal analysis technique that has been widely used to

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characterize the phase transition including crystallization, melting transition and glass transition (Koo et al., 2005; Babic et al., 2006; Ačkar et al., 2010). Analysis of DSC data can provide additional information about starch, such as its structure and composition, its interaction with other components, the effects of water, and related properties.

Even though information about starch-hydrocolloid systems exists, there are still unknown aspects because of the complexity of such systems. It is generally accepted that each hydrocolloid affects pasting properties of starch in a different way (Bahnassey and Breene, 1994; Rojas et al., 1999). This can be attributed to many factors, mainly the molecular structure of hydrocolloids and/or ionic charges of both starches and hydrocolloids (Sudhakar et al., 1995; Shi and BeMiller, 2002).

The aim of this research was to examine the effect of galactomannan hydrocolloids (guar gum and locust bean gum) on the gelatinization and retrogradation of tapioca and corn starch. In this study DSC has been used to characterise the modifications that starch gelatinization and retrogradation undergo by addition of hydrocolloids.

Materials and Methods

Materials

Tapioca starch (moisture content 13.6 %) was obtained from International Starch Trading, Aarhus, Denmark. Corn starch (moisture content 8.61 %) was obtained from Agrana, Austria. Locust bean gum (moisture content 12.37 %) and guar gum (moisture content 9.29 %) were products of Giulini Chemie, Ludwigshafen, Germany.

Methods

Gelatinization and retrogradation properties were analyzed using differential scanning calorimeter DSC 822^e (Mettler Toledo) equipped with STAR^e software. An empty pan was used as a reference. Tapioca or corn starch was weighed into standard aluminium pan (40μL). Distilled water or appropriate hydrocolloid solutions of locust bean gum or guar gum were added to the starch to give 3:7 starch:water ratio with hydrocolloids being 0.5 % or 1.25 % g/g dry starch. Pans were sealed and equilibrated for 24 h at room temperature before heat treatment in the DSC. The starch slurry was gelatinized in the DSC using a heat rate of 10 ºC/min from 25 to 95 ºC. After heat treatment, samples were cooled to 25 ºC and removed from DSC. The starch gels were aged at 4 and 25 ºC and monitored for retrogradation after 7 and 14 days. The retrogradation experiments were conducted at a heating rate of 10 ºC/min from 25 to 95 ºC. The changes in enthalpy (ΔH in J/g of dry starch), onset temperature (T_o), peak temperature (T_p) and conclusion temperature (T_c) for gelatinization and retrogradation were obtained from the exotherm DSC curves. Experiments were run in triplicates.

Statistics

Experimental data were analyzed by analysis of variance (ANOVA) and Fisher's least significant difference (LSD) with significance defined at $P<0.05$. All statistical analyses were carried out using software program STATISTICA 7 (StatSoft, Inc, USA).

Results and discussion

Tables 1 and 2 show the gelatinization characteristics of tapioca and corn starch with and without addition of hydrocolloids determined using DSC. DSC parameters recorded were onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and the gelatinization enthalpy (ΔH_g). Rojas et al. (1999) and Cameron et al. (1993) found that hydrocolloids had little or no effect on the peak gelatinization temperature of wheat and waxy maize starches. Similar results for tapioca and corn starches were obtained in this study.

Table 1. Exothermal gelatinization characteristic of tapioca starch (TS) suspensions with and without added locust bean gum (LBG) and guar gum (GG).

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_g[J/g]
TS	65.0^a±0.032	70.5^c±0.029	80.5^a±0.063	14.74^c±0.272
TS+LBG 0.5%	65.3^b±0.075	70.8^c±0.089	80.8^a±0.105	14.61^c±0.081
TS+LBG 1.25%	65.3^b±0.251	70.8^c±0.155	80.7^a±0.202	14.04^b±0.148
TS+GG 0.5%	64.9^a±0.201	70.2^b±0.186	82.6^b±0.193	14.26^{bc}±0.182
TS+GG 1.25%	64.8^a±0.081	69.8^a±0.185	86.1^c±0.066	13.28^a±0.115

Gelatinization parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_g, gelatinization enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-c) are significantly different ($P<0.05$).

Tapioca starch (TS) samples with added guar gum (GG) or locust bean gum (LBG) showed slightly higher or lower To and Tp depending on type of hydrocolloid (Table 1). To and Tp ranged from 64.8-65.3 and 69.8-70.8 ºC, respectively. This demonstrates that there was enough water available for both starch and hydrocolloid, regardless of the hydrocolloid used. GG significantly increased (P<0.05) the gelatinization conclusion temperature of TS, especially at higher concentration (86.1 ºC; control sample 80.5 ºC). Addition of hydrocolloids to TS caused a decrease in ΔHg values, which can be attributed to a reduction in water availability causing partial gelatinization of crystalline regions in starch granules and effect of starch-hydrocolloids interactions (Rojas et al., 1999; Funami et al., 2005; Chaisawang and Suphantharika, 2006). Sample with addition of GG (1.25 %) appeared to have had the lowest value ΔHg (13.28 J/g; control sample 14.74 J/g). Gelatinization enthalpies were in the range 14.04-14.61 J/g for other samples with added hydrocolloids.

Table 2. Exothermal gelatinization characteristic of corn starch (CS) suspensions with and without added locust bean gum (LBG) and guar gum (GG).

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_g[J/g]
CS	$65.1^a \pm 0.186$	$70.5^a \pm 0.178$	$76.3^a \pm 0.175$	$10.53^c \pm 0.052$
CS+LBG 0.5 %	$65.3^a \pm 0.110$	$70.2^a \pm 0.101$	$76.4^a \pm 0.182$	$10.07^b \pm 0.017$
CS+LBG 1.25 %	$65.2^a \pm 0.155$	$70.8^b \pm 0.185$	$76.9^b \pm 0.162$	$9.98^b \pm 0.104$
CS+GG 0.5 %	$65.1^a \pm 0.177$	$70.4^a \pm 0.025$	$76.3^a \pm 0.137$	$9.98^b \pm 0.064$
CS+GG 1.25 %	$64.9^a \pm 0.173$	$70.8^b \pm 0.216$	$77.7^c \pm 0.183$	$8.87^a \pm 0.095$

Gelatinization parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_g, gelatinization enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-c) are significantly different (P<0.05).

Hydrocolloids had a similar effect on corn starch (CS) gelatinization characteristics. The ΔH_g values of CS with added GG and LBG were significantly (P<0.05) lower than those of the starch alone. The T_o and T_e values, however, were unaffected or slightly changed by addition of hydrocolloids implying that the melting process of starch granules in the aqueous and hydrocolloids solutions started and completed at nearly the same temperature. Gelatinization temperatures (T_o, T_p and T_c) for corn starch with and without added hydrocolloids were in range from 64.9-65.3, 70.2-70.8 and 76.3-77.7 ºC, respectively.

Table 3. Exothermal retrogradation characteristic of tapioca starch gels, with and without added locust bean gum (LBG) and guar gum (GG), after 7 and 14 days at 4 ºC.

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_r[J/g]
After 7 days at 4ºC				
TS	$42.4^{bc} \pm 0.429$	$53.1^{ab} \pm 0.330$	$62.4^a \pm 0.410$	$4.57^d \pm 0.066$
TS+LBG 0.5%	$42.4^{bc} \pm 0.100$	$53.9^c \pm 0.211$	$62.8^a \pm 0.245$	$3.80^a \pm 0.166$
TS+LBG 1.25%	$42.5^c \pm 0.101$	$53.6^{bc} \pm 0.093$	$62.2^a \pm 0.172$	$3.98^b \pm 0.050$
TS+GG 0.5%	$42.0^b \pm 0.150$	$53.5^{bc} \pm 0.231$	$62.8^a \pm 0.112$	$3.94^b \pm 0.110$
TS+GG 1.25%	$41.0^a \pm 0.195$	$52.9^a \pm 0.252$	$62.6^a \pm 0.220$	$4.27^c \pm 0.070$
After 14 days at 4ºC				
TS	$42.4^b \pm 0.072$	$53.1^b \pm 0.177$	$62.7^b \pm 0.114$	$6.12^c \pm 0.065$
TS+LBG 0.5%	$42.1^a \pm 0.110$	$52.9^{ab} \pm 0.162$	$62.7^b \pm 0.224$	$5.76^b \pm 0.018$
TS+LBG 1.25%	$42.1^a \pm 0.216$	$53.0^{ab} \pm 0.102$	$62.7^b \pm 0.131$	$5.74^b \pm 0.100$
TS+GG 0.5%	$42.4^b \pm 0.021$	$52.7^a \pm 0.228$	$62.1^a \pm 0.227$	$5.06^a \pm 0.189$
TS+GG 1.25%	$42.4^b \pm 0.015$	$53.2^b \pm 0.257$	$62.4^{ab} \pm 0.074$	$5.53^b \pm 0.170$

Retrogradation parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_r, retrogradation enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-d) are significantly different (P<0.05).

DSC analysis has often been applied to measure starch recrystallization (retrogradation) (Funami et al., 2005; Koo et al., 2005; Babić et al., 2009). It is well known that the enthalpy of melting of recrystallized starch increases throughout storage time. Retrogradation exotherms of tapioca and corn starch with and without addition of hydrocolloids were observed after 7 and 14 days of storage at 4 and

25 ºC. The results for retrogradation parameters are shown in Table 3, 4, 5 and 6. It has been reported that retrogradation consists of two separable processes (Miles et al., 1985). The first stage is governed by the gelation of amylose solubilized during gelatinization and the second stage is induced by the recrystallization of amylopectin within the gelatinized granules. The enthalpy of melting of recrystallized starch is lower than that of gelatinization, in agreement with the fact that melting recrystallized starch during storage is always easier than melting native starch granules (Duran et al., 2001; Babić et al., 2007).

Table 4. Exothermal retrogradation characteristic of tapioca starch gels, with and without added locust bean gum (LBG) and guar gum (GG), after 7 and 14 days at 25 ºC.

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_r[J/g]
After 7 days at 25ºC				
TS	$52.3^{a}\pm0.076$	$59.8^{a}\pm0.077$	$69.3^{bc}\pm0.120$	$0.80^{c}\pm0.040$
TS+LBG 0.5%	$54.0^{c}\pm0.223$	$59.9^{a}\pm0.091$	$69.4^{c}\pm0.194$	$0.48^{ab}\pm0.016$
TS+LBG 1.25%	$54.7^{d}\pm0.091$	$59.8^{a}\pm0.017$	$68.7^{a}\pm0.120$	$0.49^{b}\pm0.061$
TS+GG 0.5%	$53.82^{bc}\pm0.205$	$59.8^{a}\pm0.025$	$69.0^{ab}\pm0.231$	$0.41^{a}\pm0.017$
TS+GG 1.25%	$53.7^{b}\pm0.179$	$59.9^{a}\pm0.085$	$69.1^{abc}\pm0.281$	$0.45^{ab}\pm0.036$
After 14 days at 25ºC				
TS	$52.2^{a}\pm0.060$	$63.0^{ab}\pm0.268$	$70.6^{cd}\pm0.341$	$1.49^{b}\pm0.151$
TS+LBG 0.5%	$54.1^{b}\pm0.031$	$63.5^{c}\pm0.085$	$70.9^{d}\pm0.044$	$1.18^{a}\pm0.004$
TS+LBG 1.25%	$54.1^{b}\pm0.021$	$63.0^{ab}\pm0.247$	$70.1^{b}\pm0.080$	$1.42^{b}\pm0.173$
TS+GG 0.5%	$55.2^{c}\pm0.236$	$63.4^{bc}\pm0.095$	$70.4^{bc}\pm0.074$	$1.10^{a}\pm0.075$
TS+GG 1.25%	$54.8^{c}\pm0.201$	$62.8^{a}\pm0.278$	$69.6^{a}\pm0.254$	$1.12^{a}\pm0.035$

Retrogradation parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_r, retrogradation enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-d) are significantly different (P<0.05).

Table 5. Exothermal retrogradation characteristic of corn starch gels, with and without added locust bean gum (LBG) and guar gum (GG), after 7 and 14 days at 4 ºC.

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_r[J/g]
After 7 days at 4ºC				
CS	$42.0^{a}\pm0.148$	$52.4^{b}\pm0.115$	$62.1^{bc}\pm0.040$	$5.03^{e}\pm0.053$
CS+LBG 0.5 %	$42.8^{b}\pm0.140$	$51.9^{a}\pm0.154$	$61.4^{a}\pm0.115$	$3.37^{b}\pm0.072$
CS+LBG 1.25 %	$43.2^{b}\pm0.032$	$52.6^{b}\pm0.292$	$61.7^{ab}\pm0.300$	$3.17^{a}\pm0.037$
CS+GG 0.5 %	$42.1^{a}\pm0.201$	$52.4^{b}\pm0.239$	$62.5^{c}\pm0.115$	$4.70^{d}\pm0.101$
CS+GG 1.25 %	$42.1^{a}\pm0.218$	$52.2^{ab}\pm0.068$	$61.8^{ab}\pm0.237$	$3.72^{c}\pm0.055$
After 14 days at 4ºC				
CS	$41.9^{a}\pm0.202$	$52.7^{b}\pm0.098$	$62.5^{c}\pm0.067$	$6.26^{d}\pm0.104$
CS+LBG 0.5 %	$42.9^{b}\pm0.036$	$52.4^{ab}\pm0.152$	$61.6^{b}\pm0.274$	$4.92^{b}\pm0.032$
CS+LBG 1.25 %	$43.1^{b}\pm0.040$	$52.2^{a}\pm0.095$	$60.5^{a}\pm0.059$	$3.88^{a}\pm0.152$
CS+GG 0.5 %	$42.8^{b}\pm0.145$	$52.8^{b}\pm0.185$	$62.2^{bc}\pm0.169$	$5.34^{c}\pm0.037$
CS+GG 1.25 %	$42.9^{b}\pm0.189$	$52.4^{ab}\pm0.225$	$62.0^{b}\pm0.035$	$5.27^{c}\pm0.033$

Retrogradation parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_r, retrogradation enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-e) are significantly different (P<0.05).

Starch-hydrocolloid interactions had influence on retrogradation of investigated samples. GG and LBG slowed retrogradation of tapioca starch gels at both investigated temperatures. GG suppressed, more than LBG, retrogradation of tapioca starch samples stored for seven and fourteen days at 25 ºC, and after fourteen days at 4 ºC (Tables 3 and 4). Samples with addition of LBG (0.5 %) had the lowest retrogradation enthalpy (ΔH_r) after seven days at 4 ºC. Generally, hydrocolloids at a lower concentration (0.5 %) had a greater effect on tapioca starch retrogradation decrease.

The results for storage at 4 and 25 ºC for one and two weeks of corn starch samples with and without addition of hydrocolloids are shown in Tables 5 and 6. Corn starch samples without addition of GG and LBG showed greater retrogradation than the samples with hydrocolloids added after 7 and 14 days of storage at both measured temperatures. The effect of hydrocolloids to decrease ΔH_r of corn starch at 4 ºC became greater in order: LBG 1.25 % (3.17 J/g) > LBG 0.5 % (3.37 J/g) > GG 1.25 % (3.72 J/g) > GG 0.5 % (4.7 J/g), after one week, and after two week: LBG 1.25 % (3.88 J/g) > GG 1.25 % (5.27 J/g) > LBG 0.5 % (4.92 J/g) > GG 0.5 % (5.34 J/g) (Table 5). Only sample with LBG (0.5 %) had significantly different (lower) ΔH_r value after 7 days of storage at 25 °C (1.08 J/g). ΔH_r of corn starch samples with GG and LBG after storage at 25 °C for two weeks ranged between 1.86 and 2.4 J/g and were significantly (P<0.05) lower than the ΔH_r of corn starch alone (Table 6).

Addition of GG and LBG increased or decreased the melting temperatures of recrystallized tapioca and corn starch depending on type and concentration of hydrocolloids, storage time and temperature of storage.

Table 6. Exothermal retrogradation characteristic of corn starch gels, with and without added locust bean gum (LBG) and guar gum (GG), after 7 and 14 days at 25 ºC.

Sample	T_o[ºC]	T_p[ºC]	T_c[ºC]	ΔH_r[J/g]
After 7 days at 25ºC				
CS	$53.0^a \pm 0.071$	$62.3^b \pm 0.180$	$69.4^a \pm 0.045$	$1.21^b \pm 0.059$
CS+LBG 0.5 %	$53.8^b \pm 0.252$	$61.9^a \pm 0.186$	$69.4^a \pm 0.166$	$1.19^b \pm 0.015$
CS+LBG 1.25 %	$54.0^b \pm 0.155$	$62.2^{ab} \pm 0.110$	$69.9^{bc} \pm 0.021$	$1.08^a \pm 0.006$
CS+GG 0.5 %	$53.7^b \pm 0.219$	$62.2^{ab} \pm 0.239$	$70.1^c \pm 0.217$	$1.20^b \pm 0.060$
CS+GG 1.25 %	$53.8^b \pm 0.208$	$61.9^a \pm 0.304$	$69.6^{ab} \pm 0.253$	$1.19^b \pm 0.007$
After 14 days at 25ºC				
CS	$53.4^a \pm 0.032$	$62.2^{ab} \pm 0.084$	$69.5^a \pm 0.029$	$2.45^d \pm 0.027$
CS+LBG 0.5 %	$54.0^b \pm 0.105$	$62.5^b \pm 0.154$	$69.9^b \pm 0.115$	$2.15^c \pm 0.072$
CS+LBG 1.25 %	$54.6^c \pm 0.062$	$62.5^b \pm 0.215$	$69.7^{ab} \pm 0.201$	$1.86^a \pm 0.107$
CS+GG 0.5 %	$53.9^b \pm 0.015$	$61.9^a \pm 0.225$	$69.6^{ab} \pm 0.055$	$2.40^d \pm 0.009$
CS+GG 1.25 %	$54.4^c \pm 0.198$	$62.3^{ab} \pm 0.166$	$69.5^a \pm 0.378$	$2.04^b \pm 0.019$

Retrogradation parameters: T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_r, retrogradation enthalpy. Values are means ±SD of triplicate. Values in the same column with different superscripts (a-d) are significantly different (P<0.05).

Conclusions

Tapioca and corn starch interaction with galactomannan hydrocolloids produces a slight modification of the differential scanning calorimetry gelatinization parameters. The addition of guar gum and locust bean gum to starches caused a decrease in gelatinization enthalpy values. Starch gelatinization temperatures were slightly lower or higher depending on type of hydrocolloid added.

Hydrocolloids slowed retrogradation of starch gels at both investigated temperatures (4 and 25 °C). Guar gum suppressed retrogradation of tapioca starch more than locust bean gum, on the other hand, locust bean gum had a greater effect on reduction of the recrystallization of corn starch.

Acknowledgements

Results shown have outcome from scientific project „Development of new modified starches and their application in food industry“, supported by the Ministry of science, education and sports of the Republic of Croatia.

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Received: February 22, 2011
Accepted: April 14, 2011