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Studies on starch–hydrocolloid interactions: effect of salts

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Starch-gum interactions offer a wide scope in food product development by virtue of their ability to modify and control the texture of foodstuffs. In many food formulations starch and hydrocolloids are used with other ingredients, e.g. salts. The present work is an attempt to study the effect of various salts such as sodium chloride, sodium sulphate, potassium chloride, calcium chloride and sodium phosphate on corn starch and xanthan combinations. The results are interpreted with respect to changes in viscosity and gelatinization temperature when the starch was pasted with xanthan (0–0·25% w/v) in the presence of salts (0–2% w/v) as measured in a Brabender amylograph. The pastes so obtained were also studied for their rheological profile on a Haake viscometer to confirm the effect under varying shear rates.

INTRODUCTION

Starch–gum interactions are widely used to modify and control the texture of various foodstuffs. Hydrocolloids such as xanthan, guar gum and carboxymethylcellulose are known to strongly influence gelatinization and retrogradation of starch (Alloncle *et al.*, 1989). The use of such combinations may also improve the heat penetration in such starch-containing canned products (Sanderson, 1982).

Starch and hydrocolloids usually co-exist with other ingredients in food formulations. One such ingredient is salt. Salts are known to regulate the swelling of starches (Ganz, 1965). Their effects on starch swelling in the presence of hydrocolloids are, however, not well understood. Thus in the present work, starch–gum interactions were studied in the presence of various inorganic salts, using a Brabender amylograph. However, since the results obtained from Brabender amylograph are at a low and fixed shear rate of about 40 s^{-1} (Wood & Goff, 1973), rheological profiling using a Haake viscometer, shear rates ranging from 100 to 1200 s^{-1} were also used to confirm the observed effect.

MATERIALS AND METHODS

Corn starch was procured from M/S Laxmi Starch Pvt. Ltd, Bombay. Food grade xanthan gum was obtained from Kelco Ltd, NJ, USA. All salts used were of AR grade.

In a total volume of 450 ml, corn starch at 5% w/v was mixed with 0–0·25% w/v xanthan gum in the presence of 0–2% w/v of various salt solutions. The salts chosen for the study were sodium chloride, potassium chloride, calcium chloride, sodium sulphate and sodium phosphate. The mixtures were heated in a Brabender amylograph (Model PT 100) from 35 to 95°C at a rate of 1·5°C min^{-1} at 75 rpm, held for 10 min at 95°C and then cooled back to 40°C. The change in behaviour was interpreted with respect to the gelatinization (pasting) temperature and cold paste viscosity at 40°C.

Rheological studies on starch, starch–xanthan combinations alone and in the presence of 2% w/v of various salts under study were also carried out using a Haake Rotovisco (Model RV3) in the shear rate range of 100 to 1200 s^{-1}. The pastes for this study were prepared by mixing the relevant ingredients and heating at 95°C for 10 min and then cooling to room temperature (30 ± 2°C). The flow behaviour index 'n' and the consistency index 'K' were calculated using a log–log plot of shear stress versus shear rate.

RESULTS AND DISCUSSION

The effect of various salts on Brabender cold paste viscosity of model starch–xanthan combinations is presented in Tables 1–3. A comparison of the cold paste viscosity values of different starch–salt models under study presented in brackets in these tables indicated that there was an increase in cold paste viscosity of 5%

starch (with respect to its value of 370 BU) when 0·5–2·0% of all five different salts were added. It was also observed that when the xanthan concentration was varied keeping the starch and salt concentration fixed, there was an increase in cold paste viscosity in most of the cases. For instance, in the case of 5% starch and 0·5% KCl, cold paste viscosity increased from 480 to 600 to 730 BU in the presence of 0·05, 0·10 and 0·25% xanthan gum, respectively. These observations can be explained as follows: in the presence of salts, starch probably exchanges cations from the solution for hydrogen ions. This results in an increase in volume of starch granules and hence an increase in viscosity. The observed increase in viscosity with increase in xanthan concentration at a fixed starch and salt concentration may be due to the facilitation of cation exchange as suggested by Oosten (1983).

At a fixed concentration of starch and xanthan gum, as the level of salt increased, there was a decrease in cold paste viscosity in most of the cases. This effect was consistent at all three levels of xanthan used in this study (Tables 1–3). Addition of salts to xanthan gum is known to reduce viscosity due to the sharp change from random coil to rigid ordered conformation (Norton *et al.*, 1984) while the addition of salt to starch increases the cold paste viscosity as observed above. Thus it appears that, in the presence of salt, the synergistic interaction of starch and xanthan gum increasing the cold paste viscosity is less effective, probably due to the conformational change in xanthan gum.

The cold paste viscosity value for 5% corn starch and 0·05% xanthan combination was 520 BU (Table 4), whereas the cold paste viscosity values for the same combination of starch and xanthan gum with any of the salts tried here, at levels of 0·5, 1·0 and 2·0%, were lower than 520 BU (Table 1). The same trend of decrease was also shown for starch–xanthan combinations at 0·1 and 0·25% (Table 4) by comparison of

Table 1. Effect of salt concentration on cold paste viscosity and gelatinization temperature of corn starch (5%)* and xanthan (0·05%)

Salt	Cold paste viscosity (BU) at salt concentration			Gelatinization temperature (°C) at salt concentration		
	0·5%	1·0%	2·0%	0·5%	1·0%	2·0%
NaCl	520 (400)	460 (460)	440 (420)	88·3 (88·0)	89·5 (89·0)	91 (91)
KCl	480 (460)	460 (400)	420 (430)	88·5 (88·5)	89·0 (89·5)	89·0 (89·5)
$CaCl_2 \cdot 2H_2O$	505 (430)	430 (390)	430 (420)	86 (86)	86 (85)	85·5 (85)
Na_2SO_4	480 (420)	510 (440)	420 (380)	90·3 (90·5)	90·3 (91)	93 (93)
NaH_2PO_4	430 (410)	475 (460)	420 (340)	88 (88)	89 (89)	89 (90·5)

*Cold paste viscosity of 5% corn starch alone is 370 BU.
Values in parentheses represent corresponding values for 5% corn starch and salt alone.

Table 2. Effect of salt concentration on cold paste viscosity and gelatinization temperature of corn starch (5%)* and xanthan (0·10%)

Salt	Cold paste viscosity (BU) at salt concentration			Gelatinization temperature (°C) at salt concentration		
	0·5%	1·0%	2·0%	0·5%	1·0%	2·0%
NaCl	505 (400)	460 (460)	490 (420)	88·0 (88·0)	89·0 (89·0)	91 (91)
KCl	600 (460)	490 (400)	440 (430)	88·0 (88·5)	89·0 (89·5)	89·0 (89·5)
$CaCl_2 \cdot 2H_2O$	520 (430)	495 (390)	420 (420)	86 (86)	86 (85)	87 (85)
Na_2SO_4	560 (420)	440 (440)	415 (380)	89·5 (90·5)	92 (91)	92 (93)
NaH_2PO_4	530 (410)	490 (460)	480 (340)	86 (88)	89 (89)	89 (90·5)

*Cold paste viscosity of 5% corn starch alone is 370 BU.
Values in parentheses represent corresponding values for 5% corn starch and salt alone.

Table 3. Effect of salt concentration on cold paste viscosity and gelatinization temperature of corn starch (5%)* and xanthan (0·25%)

Salt	Cold paste viscosity (BU) at salt concentration			Gelatinization temperature (°C) at salt concentration		
	0·5%	1·0%	2·0%	0·5%	1·0%	2·0%
NaCl	660 (400)	600 (460)	540 (420)	86·0 (88·0)	88·0 (89·0)	89 (91)
KCl	730 (460)	610 (400)	520 (430)	85·5 (88·5)	87·0 (89·5)	87·5 (89·5)
$CaCl_2 \cdot 2H_2O$	600 (430)	580 (390)	510 (420)	86 (86)	86 (85)	87·4 (85)
Na_2SO_4	750 (420)	590 (440)	545 (380)	86·0 (90·5)	89·5 (91)	91·5 (93)
NaH_2PO_4	680 (410)	650 (460)	570 (340)	85·5 (88)	86 (89)	88 (90·5)

*Cold paste viscosity of 5% corn starch alone is 370 BU.
Values in parentheses represent corresponding values for 5% corn starch and salt alone.

Table 4. Effect of addition of xanthan on the cold paste viscosity and gelatinization temperature of 5% corn starch

Ingredients	Cold paste viscosity (BU)	Gelatinization temperature (°C)
5% corn starch	370	86·6
5% corn starch + 0·05% xanthan	520	86·0
5% corn starch + 0·1% xanthan	660	82·0
5% corn starch + 0·25% xanthan	1240	74·0

the respective values in Tables 2 and 3. These results also confirm that, in combinations of starch, xanthan and salt, the effect of salt in decreasing the viscosity of xanthan gum is more pronounced than that of increasing the viscosity of starch, as previously noted.

Tables 1–3 also show that, in the case of starch and salt combination, there was an increase in gelatinization temperature as the salt concentration increased. For example, in the case of sodium chloride, the gelatinization temperature increased from 88 to 89 to 91°C as the salt concentration was increased from 0·5 to 1·0 to 2·0%. This was true in the case of all salts, except $CaCl_2 \cdot 2H_2O$ where hardly any effect was observed. These results confirm that added salts decrease the cold swelling of starch and, as the concentration of added salts increases, the cold swelling maxima are pushed to higher temperature (Tye, 1988). In addition, these observations can also probably be explained on the basis of a theory (Oosten, 1983) according to which an electrical double layer of cations surrounding the starch prevents anions penetrating so that gelatinization is also prevented. In salts, anions are known to be the actual gelatinizing agents (Oosten, 1990). In dilute solutions (or in presence of low concentration of salt), there is a decrease in electrical double layer after which anions can penetrate and cause gelatinization (Oosten, 1983). It was interesting to note that, in the absence of salts, gelatinization temperature of starch decreased with the addition of xanthan gum (Table 4). This is in accordance with an earlier report (Christianson *et al.*, 1981).

In the model combination of fixed concentration of starch and gum, gelatinization temperature increased with increasing salt concentration. This was true for all salts except $CaCl_2 \cdot 2H_2O$. For instance, in case of 5% starch and 0·05% xanthan combination, gelatinization temperature increased from 88·3 to 89·5 to 91°C when 0·5, 1·0 and 2·0% NaCl were added, respectively (Table 1). Thus in such a combination, it appears that the overall effect of increasing gelatinization temperature is due to the gum favouring the formation of an electrical double layer of cations around starch. Studies to confirm this mechanism need to be done.

In order to confirm the results obtained using the Brabender amylograph, which has a fixed configuration and shear rate (40 s^{-1}), a study of the effects of salts on starch–xanthan combinations was also attempted using a Haake viscometer at various shear rates ranging from

Table 5. Brabender cold paste viscosity (converted into cPs), flow behaviour index and consistency index of starch–xanthan combinations in the presence of various salts[a]

Parameter	Brabender viscosity (cPs)**	Flow behaviour index (*n*)	Consistency index (cPs)*
S	388·5	0·75	89·4
S + NaCl	441	0·61	501·2
S + KCl	451·5	0·60	525·1
S + $CaCl_2 \cdot 2H_2O$	441	0·60	514·3
S + Na_2SO_4	399	0·69	81·7
S + NaH_2PO_4	357	0·71	73·3
S + X_1	546	0·65	308·7
S + X_1 + NaCl	462	0·66	492·8
S + X_1 + KCl	441	0·67	467·6
S + X_1 + $CaCl_2 \cdot 2H_2O$	451·5	0·67	474·8
S + X_1 + Na_2SO_4	441	0·58	347·3
S + X_1 + NaH_2PO_4	441	0·51	518·4
S + X_2	693	0·52	1099·8
S + X_2 + NaCl	514·5	0·62	336·2
S + X_2 + KCl	462	0·62	318·9
S + X_2 + $CaCl_2 \cdot 2H_2O$	441	0·66	243·2
S + X_2 + Na_2SO_4	435	0·62	574·6
S + X_2 + NaH_2PO_4	504	0·62	595·6
S + X_3	1302	0·49	1950·9
S + X_3 + NaCl	567	0·55	759·6
S + X_3 + KCl	546	0·60	565·6
S + X_3 + $CaCl_2 \cdot 2H_2O$	535·5	0·60	555·9
S + X_3 + Na_2SO_4	572·2	0·67	363·5
S + X_3 + NaH_2PO_4	598·5	0·68	326·4

S = 5% Starch w/v.
X_1 = Xanthan gum at 0·05% w/v.
X_2 = Xanthan gum at 0·10% w/v.
X_3 = Xanthan gum at 0·25% w/v.
[a]All salts were used at 2% w/v.
* 1Pa.Sec^n = 1000 cPs.
**1 BU = 1·05 cPs.

100 to 1200 s^{-1}. Salts were used at 2% level in this study. Flow behaviour index '*n*' and consistency index '*K*' of these models were calculated using a log–log plot of shear stress versus shear rate. Since the consistency index is a measure of viscosity, the values obtained were converted into cPs for comparison with Brabender cold paste viscosities. The Brabender cold paste viscosities were also converted into cPs using the relationship, 1 BU = 1·05 cPs, under the experimental conditions of bowl speed = 75 rpm, heating rate = 1·5°C/min and cartridge used = 350 cmg. This is in accordance with an earlier report (Wood & Goff, 1973). The results so obtained are as shown in Table 5. It is clear that, in the case of starch alone, the flow behaviour index decreases from 0·75 to 0·49 with increase in xanthan gum concentration from 0·05 to 0·25%. A similar observation had been made by Sajjan and Rao (1987). Addition of salts also decreased the flow behaviour index of starch as well as starch–xanthan pastes. In the case of NaCl, the flow behaviour index decreased from 0·75 to 0·61 for starch alone and to 0·66 for starch–xanthan (0·05%) paste.

A plot of consistency index (cPs) vs Brabender cold paste viscosity (cPs) yielded a regression output (R^2 = 0·88) from which the predicted Brabender cold paste

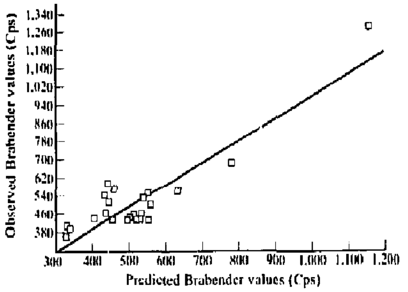

Fig. 1. Correlation between observed and predicted Brabender cold paste viscosity values.

viscosity was calculated. Figure 1 shows a plot of predicted vs observed Brabender cold paste viscosity of all the model systems, i.e starch alone, starch–salt and starch–xanthan–salt systems, under study. The close proximity of the observed Brabender values to the predicted values validates the effect of salt on starch–xanthan combinations as obtained only from a single point measurement using the Brabender amylograph. The deviation ranged from −35·7 to 20·55%.

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