Rheological properties of some starch-water-sugar systems

Marek Sikora,¹ Jozef Mazurkiewicz,² Piotr Tomasik^{3*} & Krzysztof Pielichowski⁴

1 Department of Carbohydrate Technology

2 Departmentof Physics

3 Departmentof Chemistry, University of Agriculture, 30120 Krakow, Poland

4 Independent Department of Organic Technology, Technical University, Krakow 31155, Poland

(Received 20 November 1998; Accepted in revised form 1 May 1999)

Summary When certain amounts of starch were blended with saturated, aqueous solutions of Dfructose, D-glucose or sucrose, shear thickening, easily pourable semi-solids were formed. The amount of starch necessary to cause this rheological effect depended, at least in part, on the starch variety. The conditions necessary to observe this effect using potato and corn starch blends with D-fructose, D-glucose and sucrose are presented. This method may be useful in studies of starch granule morphology. Gelation characteristics and differential scanning calorimetry (DSC) of potato and corn starch in saturated aqueous Dfructose, D-glucose, and sucrose solutions showed that both starch varieties interacted differently with the environment. Starch more readily gelatinised in sucrose solutions than in solutions of D-fructose and D-glucose.

Keywords Corn starch, differential scanning calorimetry, diffractometry, potato starch, shear thickening.

Introduction

Physical and chemical properties of starch significantly depend on structure and properties of its granules. In spite of novel discoveries in the starch granule organization (Gallant *et al.*, 1997; Starzyk *et al.*, 1998) there are few methods available for the estimation of the ability of granules to be penetrated by solvents and reagents. The method presented in this paper is based on the competition for water molecules between starch granules and D-fructose, D-glucose, and sucrose for water molecules. This method might also be suitable for the determination of technological value of starch varieties in certain methods of their processing.

At low water contents, food components com-

*Correspondent: Voice: +48 12 63388; Fax: +48 26 48 12 63362; e-mail: rrtomasi@cyf-kr.edu.pl

© 1999 Blackwell Science Ltd

pete for water molecules. The varying conditions of food processing and storage influence the results of this competition. Therefore, a number of workers have studied the organization of water and its mobility in starch and food components. Starch - sugar blends were also investigated (Lim et al., 1992a; Lim et al., 1992b; Kulik et al., 1994; Prokopovich & Biliaderis, 1995). Considerable attention has been paid to the plasticizing role of water in the starch - sugar - water systems (Collison & Chilton, 1974; Bean et al., 1978; Donovan, 1979; Biliaderis et al., 1980; Eliasson, 1980; Ghiashi et al., 1982; Spies & Hoseney, 1982; Burt & Russell, 1983; Chungcharoen & Lund, 1987). Usually, in these studies the starch : sugar : water ratio did not exceed 1.0 : 0.5 : 1.5 (w/w) (Prokopovich & Biliaderis, 1995), and only one report (Chinachoti, 1993) described properties of a starch-sugar-water blend in which the ratio of these components was close to 1 : 0.5 : 0.5, respectively. The peculiar rheological properties of the latter blend were named 'the magic trick'. The semi-solid blend could be easily poured from a beaker. The phenomenon was a particular case of shear thickening behaviour described by a general Herschel-Bulkley model for viscoelastic systems (Steffe, 1996). Other systems exhibiting this effect include some types of honey and a 40% raw maize starch dispersion (Steffe, 1996).

In our opinion using granular starch this effect might be time-dependent, and therefore, useful in studies of the morphology of starch granules and their functional properties. For example, there could be differences in observed rheology, caused by the penetration of sugar molecules into the interior of starch granules. Penetration into amorphous regions of granules was documented by Brown & French (1977), and the formation of starch complexes with lower sugars was shown by Tomasik *et al.* (1995).

Increases in gelatinization temperature are sugar-concentration dependent. The explanation

Table 1 Dynamic viscosity, DV, and flow rate, FR, at constant shear stress (250 G/cm²) for various proportions of corn starch: D-fructose: water in the

blends

of this phenomenon (Evans & Haisman, 1982; Slade & Levine, 1982; Spies & Hoseney, 1982; Kohyama & Nishinari, 1991; Larsson & Eliasson, 1991) has been given recently by Beleia et al. (1996). They demonstrated that water inside the starch granule was displaced. Moreover, water had decreased activity. However, this conclusion was valid for aqueous solutions in which the sugar concentration did not exceed 50 w/w% (Collison & Chilton, 1974; Beleia et al., 1996; Bean et al., 1978; Bean & Yamazaki, 1978; Donovan, 1979; Biliaderis et al., 1980; Eliasson, 1980; Ghiashi et al., 1982; Burt & Russell, 1983; Chungcharoen & Lund, 1987; Chinachoti & Stengle, 1990; Kim & Walker, 1992; Lim et al., 1992a, 1992b; Hoover & Senanyake, 1996; Prokopovich & Biliaderis, 1995). Only Johnson et al. (1990) presented data on starch gelatinization in sugar solutions containing a water content of 11%. In this paper, gelatinization of starchsugar-water blends in which the ratio of components was close to 1:0.5:0.5 was studied and the properties of gels given.

Starch: aq. sat. D-fructose ^b , w/v	FR, 10 ⁻⁴ after	FR, 10 ^{−4} cm/s after			DV, Pa.s after			
	0h	1h	3h	0h	1h	3h		
			20 °C					
1:0.90	1035	556	543	483	900	920		
1:0.95	437	250	145	1144	2000	3450		
1:1.00	250	55	ev°	2000	9150			
1:1.05	71	32	ev	7025	15800			
			30 °C					
1:0.90	926	340	204	540	1470	2450		
1:0.95	625	215	101	800	2582	4953		
1:1.00	556	109	ev	900	4600			
1:1.05	69	49	ev	7250	10125	ev		
			40 °C					
1:0.90	5000	1000	ev	100	500			
1:0.95	2632	625	ev	190	800			
1:1.00	400	ev	ev	1250	ev			
1:1.05	238	ev	ev	2100	ev			
			50 °C					
1:0.90	2500	ev	ev	200	ev	Εv		
1:0.95	2083	ev	ev	240	ev	Εv		
1:1.00	1316	ev	ev	380	ev	ev		
1:1.05	521	ev	ev	960	ev	ev		

^aThe estimated average error is $\pm 4.5\%$

^bThe solutions of 1g of D-fructose in 0.5g of water were used.

°The effect vanished.

International Journal of Food Science and Technology 1999, 34, 371-383

 Table 2 Dynamic viscosities, DV,

 and flow rate, FR, at constant

 shear stress (250 G/cm²) for

 various proportions of corn

 starch: D-glucose: water in the

 blends^a

Starch: aq. sat. D-glucose ^ь , w/v	FR, 10 ^{-/} after	FR, 10 ^{−4} cm/s after			DV, Pa.s after		
	0h	1h	3h	0h	1h	3h	
			20 °C				
1:1.00	1039	520	437	489	962	1151	
1:1.05	241	411	298	1073	1216	1679	
1:1.10	ev°	ev	ev	ev	ev	ev	
			30 °C				
1:1.00	1313	854	460	381	562	1087	
1:1.05	537	471	306	932	1062	1636	
1:1.10	420	ev	ev	1192	ev	ev	
1:1.15	ev	ev	ev	ev	ev	ev	
			40 °C				
1:1.00	2219	1783	860	225	280	581	
1:1.05	786	745	662	636	671	756	
1:1.10	444	400	352	1127	1251	1421	
1:1.15	307	293	280	1627	1706	1786	
			50 °C				
1:1.00	2200	2170	989	225	230	506	
1:1.05	1350	1296	662	370	385	756	
1:1.10	641	602	520	780	830	961	
1:1.15	387	349	281	1292	1432	1782	

<code>aThe estimated average error is $\pm 5.0\%$ </code>

^bThe solutions of 1g of D-fructose in 1g of water were used.

°The effect vanished.

 Table 3 Dynamic viscosities, DV

 and flow rate, FR, at constant

 shear stress (250 G/cm²) for

 various proportions of corn

 starch: suctrose: water in the

 blends^a

Starch: aq. sat. sucrose ^ь , w/v	FR, 10 ^{-₄} after	cm/s		DV, Pa.s after		
	0h	1h	3h	0h	1h	3h
			20 °C			
1:0.80	6234	5714	5005	89	88	100
1:0.85	4440	4357	3128	113	115	160
1:0.90	1087	1020	552	460	490	905
1:0.95	227	138	112	2200	3620	4460
			30 °C			
1:0.80	12488	8000	7146	40	63	70
1:0.85	6663	5720	5131	75	87	97
1:0.90	1641	1335	1220	305	374	410
1:0.95	623	313	137	803	1600	3660
			40 °C			
1:0.80	25000	11111	4363	20	45	115
1:0.85	12500	5885	962	40	85	520
1:0.90	4262	1873	199	117	267	2510
1:095	2280	1213	167	219	412	3000
			50 °C			
1:0.80	22244	15392	888	22	32	563
1:0.85	12506	2854	325	40	175	1540
1:0.90	3330	658	86	150	760	5820
1:0.95	2439	433	evc	205	1156	ev

<code>aThe estimated average error is $\pm 6.0\%$ </code>

^bThe solutions of 1g of suctrose in 0.5g of water were used.

°The effect vanished.

Table 4 Dynamic viscosities, DV, and flow rate, FR, at constant shear stress (250 G/cm²) for various proportions of potato starch: D-fructrose: water in the blends^a

Starch: aq. sat.	FR, 10 ^{-₄} after	FR, 10 ^{−4} cm/s after			DV, Pa.s after			
D-fructose⁵, w/v	0h	1h	3h	0h	1h	3h		
			20 °C					
11:1.00	11765	7696	7415	43	65	67		
1:1.05	9114	7415	6256	55	67	80		
1:1.10	7404	5561	5003	68	90	100		
1:1.15	4006	3846	3340	125	130	150		
1:1.20	1536	1332	1053	325	375	475		
			30 °C					
1:1.00	20010	16675	15423	25	30	32		
1:1.05	12494	11139	10101	40	45	50		
1:1.10	10000	8004	6663	50	62	75		
1:1.15	8346	7996	3452	60	63	145		
1:1.20	5261	4764	3337	95	105	150		
			40 °C					
1:1.00	33333	25025	392	15	20	1275		
1:1.05	25013	24988	ev°	20	20	e\		
1:1.10	20000	18191	ev	25	27	ev		
1:1.15	16667	15385	ev	30	33	ev		
1:1.20	16675	14293	ev	30	35	ev		
			50 °C					
1:1.00	40040	14293	ev	13	35	ev		
1:1.05	25025	1100	ev	20	455	ev		
1:1.10	20010	1031	ev	25	485	ev		
1:1.15	18182	417	ev	28	1200	ev		
1:1.20	13340	ev	ev	37	ev	e١		

^aThe estimated average error is \pm 4.25%

^bThe solutions of 1g of D-fructose in 0.5g of water were used.

°The effect vanished.

Materials and methods

Materials

Potato starch was isolated and provided by Potato Starch Enterpise in Lomza (Poland) in 1997. Corn starch was the product of B.V. Melunie Flour & Starch Union, Amsterdam (The Netherlands).

Commercial sucrose was obtained from the Sugar Factory Chybie S.A. (Poland), anhydrous D-glucose was manufactured by Polish Chemicals POCh in Gliwice, and fructose was obtained from Sigma, St Louis, MO (USA). Water was redistilled.

Methods

Aqueous solutions of D-fructose, D-glucose and sucrose, all saturated at room temperature, were combined with either corn or potato starch to give the ratios shown in Table 1. These blends were subjected to consistometric studies, in the temperature range from 20 to 50 °C at 10 °C intervals, immediately after sample preparation. The dynamic viscosity and shear rate at constant shear stress of 250G/cm² were measured as a function of time immediately after the samples were prepared. A Hoeppler KO-type consistometer (VEB Pruefgeraete, Medingen, Germany), coupled with a thermostat providing temperature maintenance to ± 0.5 °C was used in the investigation. The measurements were triplicated.

X-Ray powder diffractograms were recorded for plain starch varieties as well as for starch (1g) soaked for 24 hours in saturated aqueous D-fructose, D-glucose and sucrose solutions (25 ml). The samples were studied after filtration, washing the filter with cold distilled water (25 ml), and drying in a dessicator over P_2O_5 . A Phillips PW 1710 diffractometer (Phillips, Eindhoven, The Netherlands) with copper radiation was used with θ angle scanned from 5 to 60 °. Gelation characteristics were analyzed using the Brabender Amylograph following the standard programme, this consists of temperature increase from 20 to 96 °C, at a rate of 1.5 °C min⁻¹ followed by 20 min storage at 96 °C and cooling to 50 °C at the same rate as heating. These characteristics were measured for 5.9% w/w (corn starch) and 3.2% w/w (potato starch) aqueous suspensions, as well as for suspensions of starch (28.18 g), in saturated aqueous solutions of either D-fructose, D-glucose, or sucrose (subsequently 17.22, 18.94, 40.0, 80.0 and 150g of such solutions) and distilled water (added to a final volume of 400 ml). The measurements were duplicated.

We used differential scanning calorimetry to measure the starch (20 mg) suspensions in water and sugar solutions listed in Table 1. Netzsch DSC 200 apparatus (Germany) was used. A weight ratio of 1 : 3 starch to water or saturated aqueous sugar solution was always maintained. Additionally, all measurements were also done for aqueous starch suspensions containing the same amount of water as in the blends containing saturated sugar solutions. Freshly prepared samples as well as starch samples soaked in sugar solutions for 24 hours were measured. In every case the rate of the temperature increase was 10 °C min⁻¹ and the measurement range was from 20 to 200 °C. All DSC measurements were triplicated.

Results and discussion

The rheological "magic trick", strong shear thickening, manifested by the highest possible flow rate of the consistometer ball (FR), ν , and the lowest possible dynamic viscosity (DV), η . Overdosing the saturated aqueous solution of sugar reduced FR and increased DV as shown in Table 1. The observed effect and its magnitude were dependent on starch variety, type of sugar in the saturated aqueous solution, time, and temperature. Table 1–6 present FR and DV measured at constant shear stress for blends of potato and maize starch with D-fructose, D-glucose or sucrose. At 20 °C the "magic trick" thickening effect was observed at a sugar-to-starch ratio of

Starch: aq. sat. ɒ-glucose ^ь , w/v	FR, 10 ^{-₄} after	cm/s		DV, Pa.s aft	er		
	0h	1h	3h	0h	1h	3h	
			20 °C				
1:0.90	9519	7146	4260	53	70	117	
1:0.95	4004	4004	3082	125	125	162	
1:1.00	1587	1724	263	315	290	1900	
1:1.05	429	199	ev°	1165	2513	ev	
1:1.10	134	ev	ev	3743	ev	ev	
			30 °C				
1:0.90	20000	19980	7150	25	25	70	
1:0.95	8704	4764	4663	57	105	107	
1:1.00	4255	1738	9090	118	288	550	
1:1.05	2947	800	714	170	625	700	
			40 °C				
1:0.90	33367	33417	14307	15	15	35	
1:0.95	16675	9995	9514	30	50	53	
1:1.00	10532	5885	4004	48	85	125	
1:1.05	3447	1048	871	145	477	574	
			50 °C				
1:0.95	33400	11111	8704	15	45	57	
1:1.00	33333	8000	7139	15	63	70	
1:1.05	9514	4653	2300	53	107	217	
1:1.10	8004	3571	212	62	140	2360	

^aThe estimated average error is $\pm 4.75\%$

^bThe solutions of 1g of D-glucose in 1g of water were used.

°The effect vanished.

International Journal of Food Science and Technology 1999, 34, 371-383

Table 5 Dynamic viscosities, DV, and flow rate, FR, at constant shear stress (250 G/cm²) for various proportions of potato starch: D-glucose:water in the blends^a 1: 1.00, 1: 0.90 and 1: 1.00 for D-fructose, Dglucose and sucrose, respectively. Both factors describing the "magic trick", i.e. FR and DV, varied relatively slightly with decrease of the sugar-to-starch ratio for D-fructose and sucrose, whereas for D-glucose such changes were more pronounced. For the blends with maize starch the "magic trick" e. g. thickening effect appeared at a sugar-to-starch ratio of 1: 0.90, 1: 1.00 and 1 : 0.80 for D-fructose, D-glucose and sucrose, respectively. The maize starch blend with sucrose was the least sensitive to composition changes but it still significantly exceeded that observed for the potato starch blends. The stabilization time of particular blends varied for particular systems. FR and DV changed within the first hour after blending, and within the next two hours they changed fairly slightly. The rate of this increase was also dependent on the sugar-type. For potato starch at 20 °C, at the thickening point and within the first hour after blending, FR decreased

by approximately 35, 25 and 3% and DV increased by approximately 53, 33 and 3%, for blends with D-fructose, D-glucose and sucrose, respectively. For maize starch blended with these sugars, FR decreased and DV increased by 46, 50 and 8% and 86, 97 and 9%, respectively. Temperature increase acted cooperatively with the FR increase and DV decrease and, simultaneously, extended the starch-to-sugar ratio in which the "magic trick" could be observed. Figure 1, the variation of shear stress (SS), τ , with FR for maize starch - sucrose compositions shows the effect of composition varying from 1 : 1 to 1 : 1.11 upon the effect under study. FR decreased as the starch : glucose ratio decreased. The blend viscosity increased with the amount of saturated glucose solution added. Analysing the data on a logarithmic scale provided the Herschel-Bulkley factor, n, in Eqn. 1.

$$\tau = \nu^n + \tau_o \tag{1}$$

Table 6 Dynamic viscosities, DV, and flow rate, FR, at constant shear stress (250 G/cm²) for various proportions of potato starch: sucrose: water in the blends^a

Starch: aq. sat. sucrose ^ь , w/v	FR, 10 ^{-₄} after	cm/s		DV, Pa.s after		
	0h	1h	3h	0h	1h	3h
			20 °C			
1:1.00	10450	10140	7000	48	49	71
1:1.05	10160	9120	5070	49	55	99
1:1.10	6760	5080	ev°	74	98	ev
1:1.15	3580	2080	ev	140	240	ev
1:1.20	1550	520	ev	323	962	ev
			30 °C			
1:1.00	23750	23730	28440	21	21	28
1:1.05	25360	17800	13130	25	28	38
1:1.10	17790	16810	5480	28	30	91
1:1.15	6940	7300	2150	72	78	233
1:1.20	3060	2500	ev	163	200	ev
			40 °C			
1:1.00	32370	24210	480	15	21	1042
1:1.05	27700	20220	160	18	31	3125
1:1.10	24170	10760	ev	21	46	ev
1:1.15	16160	1720	ev	31	201	ev
1:1.20	4820	290	ev	104	1724	ev
			50 °C			
1:1.00	34000	ev	ev	12	ev	ev
1:1.05	31000	ev	ev	16	ev	ev
1:1.10	30950	ev	ev	16	ev	ev
1:1.15	24760	ev	ev	20	ev	ev
1:1.20	2060	ev	ev	243	ev	Εv

^aThe estimated average error is $\pm 6.25\%$

^bThe solutions of 1g of sucrose in 0.5g of water were used.

°The effect vanished.

International Journal of Food Science and Technology 1999, 34, 371-383

where τ_{o} , the yield stress, is equal to zero for Newtonian liquids and is above zero for Bingham liquids. This parameter characterizes rheological properties of the blends under study. However, the small number of experimental points as well as the low precision of the method made estimated values uncertain. Since

$$\tau = \eta \nu + \tau_{o} \tag{1}$$

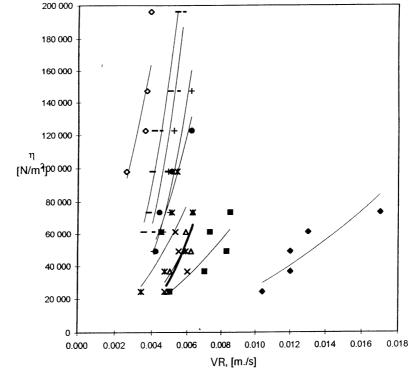
an increase in SS and n-coefficient in Eqn. 1 is paralleled by the viscosity increase. Figure 2 shows selected examples of non-linear viscosity – FR relationships. Figure 3 presents the non-linear viscosity increase against the increase of the volume of sugar solution added. This non-linearity might reflect the result of the competition for water molecules which vanishes altogether with the thickening effect, due to apparent drying of the blend. This effect could result from the penetration of the starch granules by water and sugar molecules. Our observations implied that sugarwater–starch interactions depended on the starch variety and sugar. Starch and saccharide competed for deficient water molecules and when starch

Figure 1 The shear stress (SS) -flow rate (FR) relationships for corn starch – saturated aqueous. glucose solution blends containing the later in the varying proportions of starch : aqueous saturated sugar solution. Sucrose : starch proportions are as follows: $\blacklozenge -1:1; \blacksquare -1:1.01;$ $\Delta -1:1.02; \times -1:1.03;)(-1:1.05;$ $\blacksquare -1:1.06; + -1:1.07; -1:1.08;$ $-01:1.09; \diamond\} - 1:1.0.$ took control over them the blend apparently dried.

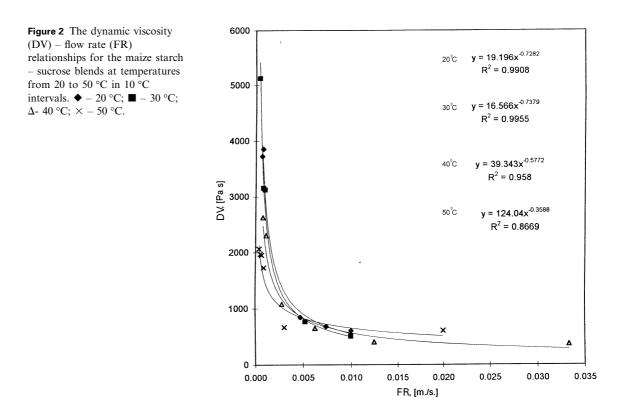
The temperature increase accelerated drying and thickening ceased as shown in Table 1–6 and Fig. 2.

Generally, to perform the "magic trick" with maize starch, less saturated D-fructose and sucrose solutions were needed than for the same effect with potato starch. The opposite effect was observed for D-glucose solutions. At the "magic trick" point and lower starch-to-sugar ratios, the maize starch blends had, by almost one order of magnitude, lower FR and, almost one order of magnitude higher DV than the corresponding blends of potato starch. The "magic trick" ceased with time and temperature more quickly using corn than potato starch blends. These observations reflect the differences in granules of both starch varieties in their ability to swell and entrap water molecules in their interiors.

Comparison of the diffractograms (Fig. 4 and 5) provided evidence that sugars indeed penetrated into the starch granules. In both diffractograms there is a difference between the patterns for starch dried in the blend with saturated aque-



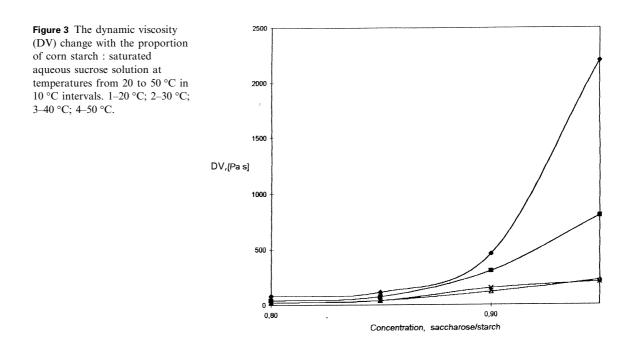
International Journal of Food Science and Technology 1999, 34, 371-383



ous solution of a saccharide (3), original starch (2) and pure sugar (1), particularly in the ranges of $2\theta = 19-20^{\circ}$ and $24-25^{\circ}$.

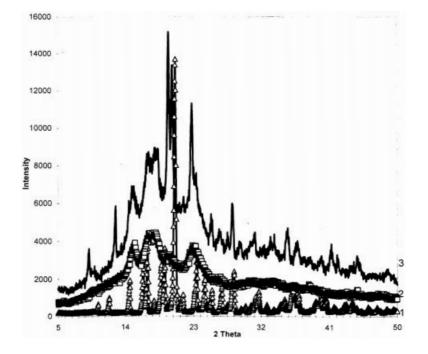
tics of corn and potato starch, respectively, in saccharide solutions of increasing concentration whilst maintaining a constant concentration of starch. There was a typical difference in the gela-

Figures 6 and 7 show the gelation characteris-



International Journal of Food Science and Technology 1999, 34, 371-383

Figure 4 Diffractograms of crystalline d-glucose (1), corn starch (2) and the dried corn starch – saturated aqueous. D-glucose solution blend (1:1.05) (3).



tion characteristics of tuber and cereal starches, although the characteristic behaviour for potato starch in the current experiments for 3.2% w/w suspensions differed from that for 7.2% w/w suspensions in water (published elsewhere e.g. by Mazurs *et al.*, 1957). The effect of sugar on the gelation temperature of both starches was slight-

ly different. For corn starch, D-fructose and Dglucose decreased the gelation temperature slightly and sucrose had, practically, no effect (Fig. 6). The gelatinization temperature of potato starch always increased with the addition of sugar (Fig. 7). This increase was roughly proportional to the sugar concentration. Regardless of the con-

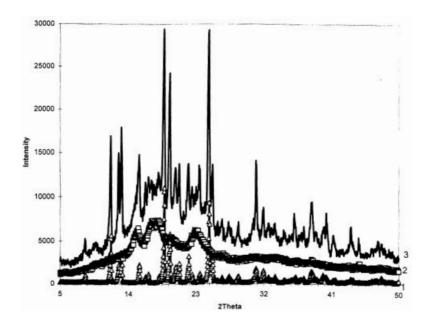
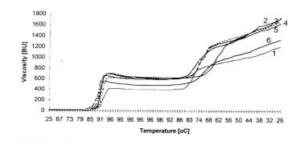
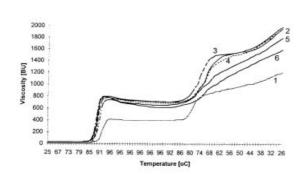


Figure 5 Diffractograms of sucrose (1), corn starch (2) and dried corn starch – saturated aqueous. sucrose solution blend (1:1.05) (3).

© 1999 Blackwell Science Ltd

International Journal of Food Science and Technology 1999, 34, 371-383





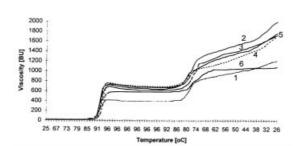


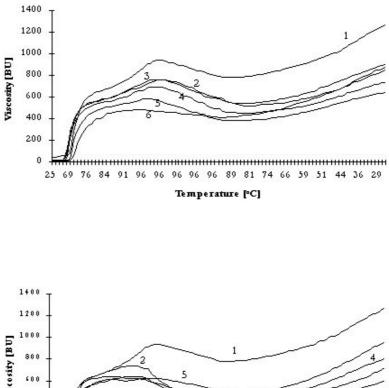
Figure 6 Gelation characteristics of the corn starch blends (5.9% w/w) with varying proportions of saturated aqueous solution added (a-d-fructose solution; b-D-glucose solution; c – sucrose solution). 1 – No sugar; 2–17.22 g of sugar; 3–18.94 g of sugar; 4–40.0 g of sugar; 5–80.0 g of sugar; 6–150.0 g of sugar in 400 ml of gelatinized starch suspension.

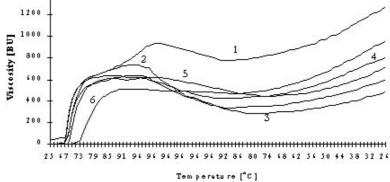
centration of sugars in the solution, the viscosity of the corn starch gels was higher than that of the gel produced in water as shown in Fig. 6. There was an opposite trend for the potato starch gels (Fig. 7). Their viscosity decreased with increasing sugar concentration in the solution, regardless of the type of sugar used. These observations are related to the water availability for penetration and also sugar transport to the granule interior. The viscosity of the corn gel during cooling was always higher when the gel was produced in sugar solution. However, it decreased with increasing sugar concentration for all three sugars. The behaviour of the potato starch gels was the opposite. D-fructose and D-glucose caused a noticeable decrease in gel viscosity but sucrose had a very small effect on it.

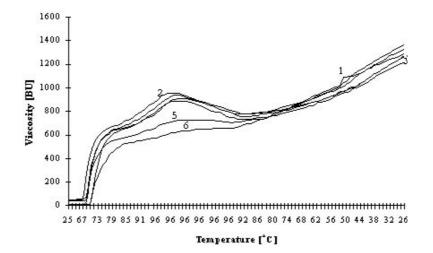
The results of the differential scanning calorimetry measurements (DSC) (Table 7) showed that within 24 h storage of starch of both varieties in saturated D-fructose and D-glucose solutions, the onset temperatures (Tonset) only slightly increased whereas such storage with the sucrose solutions resulted in a clear decrease in onset temperature. This indicated that starch had a higher affinity for water in the presence of sucrose compared to Dfructose and D-glucose. Sucrose has the lowest osmotic activity among the three sugars tested. Data for both starch varieties were consistent with the data from rheological studies. All showed that corn starch was always more readily hydrated and more readily swelled than potato starch. Gelatinization enthalpies (Δ H) showed that during gelatinization of corn starch granules, water was least available from the D-fructose solution and most available from the sucrose solution. However, gelatinization enthalpies after 24 h soaking in sugar solutions suggested that sucrose penetrated granule interiors most and D-fructose least. Such penetration produces disorder inside the granules. Based on the same criteria, the potato starch granules were almost equally well hydrated by water from all three sugar solutions and equally penetrated by all three sugars. Experiments were also done with gelatinization of both starch varieties under the same formal water availability as in the experiments with sugar solutions, since as sugars were not added, the total water was free for interactions with starch. The enthalpies for potato starch were by 0.5 to one order of magnitude higher than those for corn starch. It is interesting that enthalpy changes were not proportional to the water content. In corn starch granules the median amount of water caused the structure to strengthen, whereas in potato starch granules the same amount of water deteriorated the granule structure.

Conclusion

Rheological properties of shear thickening semisolids obtained by blending of starches with satuFigure 7 Gelation characteristics of the potato starch blends with varying proportions of saturated aqueous sugar solution added (a–D-fructose; b–D-glucose; c – sucrose solution). 1 – No sugar; 2–17.22 g of sugar; 3–18.94 g of sugar; 4–40.0 g of sugar; 5–80.0 g of sugar; 6–150.0 g of sugar in 400 ml of gelatinized starch suspension.







International Journal of Food Science and Technology 1999, 34, 371-383

Starch	Sugar	Time of runa	$\mathbf{T}_{onset},^{\circ}\mathbf{C}^{b}$	$T_{peak'}^{\circ}C^{c}$	$\mathbf{T}_{end}, \mathbf{C}^{d}$	ΔH , J/g ^e
Corn	None ^f	0	67.0	97.8	119.8	286.8
			130.0	132.9	142.0	353.4
			65.2	94.5	124.0	431.4
	Fru	0	116.7	123.9	145.1	90.1
		24	118.5	126.3	143.5	91.7
	Glu	0	64.5	98.0	126.8	84.59
		24	66.6	104.2	135.9	42.8
	Suc	0	65.0	98.3	135.2	63.7
		24	58.3	87.4	117.7	41.0
Potato	None ^f	0	145.7	172.5	177.8	2166
			100.0	145.6	151.2	2319
			104.8	139.7	142.2	1809
	Fru	0	117.6	130.1	162.4	86.3
		24	118.0	134.9	163.3	41.4
	Glu	0	62.2	99.4	128.8	83.8
		24	66.9	99.3	163.3	41.4
	Suc	0	79.3	102.2	130.5	93.0
	24	58.2	81.1	118.3	45.1	

Table 7 Results of DSC measurements of corn and potato starch in pure water and in saturated aqueous sugar solutions

^aThe samples were subjected to measurements immediately after blending (0h) or after 24 hours from the moment of blending. The estimated average error in DSC measurements did not exceed \pm 11.2%.

^bThe onset temperature.

°The peak temperature.

^dThe end temperature.

°The enthalpy differences of the glassy transition.

Three sets of values run without sugar addition relate to the aqueous starch blends containing the same amount of water as in the blends with aqueous sugar solutions. The starch:water ratio 1:0.28, 1:1.09, and 1:0.50 correspond to the amount of water in the starch blended with saturated aqueous d-fructose (Fru), d-glucose (Glu), and sucrose (Suc)solutions, respectively. In the Table the data for sugar-free aqueous starch suspensions are listed in above sequence.

rated aqueous solutions of mono- and di-saccharides depend on starch variety and saccharide in saturated solution. These observation may be useful in studies of the morphology of starch granules.

References

- Bean, M.N. & Yamazaki, W.T. (1978). Wheat starch gelatinization in sugar solutions. I Sucrose: Microscopy and viscosity effects. *Cereal Chemistry.*, 55, 936–944.
- Bean, M.N., Yamazaki, W.T. & Donelson, D.H. (1978a). Wheat starch gelatinization in sugar solutions. II. Fructose, glucose, sucrose, cake performance. *Cereal Chemistry.*, 55, 945–951.
- Beleia, A., Miller, R.A. & Hoseney, R.C. (1996). Starch gelatinization in sugar solutions. *Starch/die Staerke*, 48, 259–262.
- Biliaderis, C.G., Maurice, Y.J. & Vose, J.R. (1980). Starch gelatinization phenomena studied. *Journal of Food Science*, **59**, 203-212.
- Brown, S.A. & French, D. (1977). Specific adsorption of starch oligosaccharides in the gel phase of starch granules. *Carbohydrate. Research.*, **59**, 203–212.

- Burt, D.J. & Russell, P.L. (1983). Gelatinization of low water content wheat starch – water mixtures. *Starch/die Staerke*, **35**, 354–360.
- Chinachoti, P. (1993). Water mobility and its relation to functionality of sucrose-containing food systems. *Food Technology (Chicago)*, **47**, 134–140.
- Chinachoti, P. & Stengle, T.R. (1990). Water mobility in starch/sucrose systems: an oxygen NMr study. *Journal* of Food Science., 55, 1732–1734.
- Chungcharoen, A. & Lund, D.B. (1987). Influence of solutes and water on rice starch gelatinization. *Cereal Chemistry.*, 64, 240–243.
- Collison, R. & Chilton, W.G. (1974). Starch gelation as a function of water content. *Journal of Food Technology.*, 9, 309–315.
- Donovan, J.W. (1979). Phase transitions of the starch water systems. *Biopolymers*, 18, 263–275.
- Eliasson, A.C. (1980). Effect of water content on the gelatinization of wheat starch. *Starch/die Staerke*, 32, 270–272.
- Evans, I.D. & Haisman, D.R. (1982). The effect of solutes on the gelatinization temperature range of potato starch. *Starch/die Staerke*, **34**, 224–231.
- Gallant, D.J., Bouchet, B. & Baldwin, P.M. (1997). Microscopy of starch: evidence of a new Level of

International Journal of Food Science and Technology 1999, 34, 371-383

granule organization. *Carbohydrate. Polymers*, **32**, 177–191.

- Ghiashi, K., Hoseney, R.C. & Varriano-Marston, E. (1982). Gelatinization of wheat starch III. Comparison by differential scanning calorimetry and light microscopy. *Cereal Chemistry*, **59**, 258–262.
- Hoover, R. & Senanyake, N. (1996). Effect of sugars on the thermal and retrogradation propoerties of oat starches. *Journal of Food Biochemistry*, 20, 65–83.
- Johnson, J.M., Davies, E.A. & Gordon, J. (1990). Interactions of starch and sugar water measured by electron spin resonance and differential scanning calorimetry. *Cereal Chemistry*, 67, 286–291.
- Kim, C. S. & Walker, C. E. (1992). Effects of sugars and emulsifiers on starch gelatinization evaluated by differential scanning calorimetry. *Cereal Chemistry*, 69, 212–217.
- Kohyama, K. & Nishinari, K. (1991). Effect of soluble sugars on gelatinization and retrogradation of sweet potato starch. *Journal of. Agriculture and Food Chemistry*, **39**, 1406–1410.
- Kulik, A.S., Chris de Costa, J.R. & Haverkamo, J. (1994). Water organization and molecular mobility in maize starch investigated by two-dimensional solid state NMR. *Journal* of. *Agricultural and Food Chemistry*, **42**, 2803–2807.
- Larsson, I. & Eliasson, A.-C. (1991). Anneling of starch at an intermediate water content. *Starch/die Staerke*, 43,

227-231.

- Lim, H., Setser, C.S. & Paukstelis, J.V. (1992a). Comparison of water mobility using 17O nuclear magnetic resonance for four sugars: glucose, maltose, maltotriose, and sucrose. *Cereal Chemistry*, **69**, 387–390.
- Lim, H., Setser, C.S., Paukstelis, J.V. & Sobczynska, D. (1992b). 17O Nuclear magnetic resonance studies on wheat starch-sucrose-water interactions with increasing temperature. *Cereal Chemistry*, 69, 382–386.
- Mazurs, E.G., Schoch, T.J. & Kite, F.E. (1957). Graphical analysis of the Brabender viscosity curves of various starches. *Cereal Chemistry*, 34, 141–152.
- Prokopovich, D.J. & Biliaderis, C.G. (1995). A comparative study of the effect of sugars on The thermal and mechanical properties of concentrated waxy maize, wheat, potato, and pea starch gels. *Food Chemistry.*, 52, 255–262.
- Slade, L. & Levine, H. (1982). Industrial Polysaccharides. (eds. S. S. Stevala, V. Crescenzi, & I. C. M. Dea). Pp. 387–430. New York: Gordon and Breach.
- Spies, R.D. & Hoseney, R.C. (1982). Effect of sugars on starch gelation. *Cereal Chemistry*, 59, 128–131.
- Starzyk, F., Polaczek, E. & Tomasik, P. (1998). Novel optical phenomena in starch granules observed in crossed polarized and non-polarized light beams. *Proceedings of the, V. I. I. International Starch Convention, Cracow*, 16–11 June 1998. P. 53. Krakow, Poland: University of Agriculture.