Crystals in Hard Candies

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Abstract

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The main purpose of the contribution presented here is the study of the glassy state and the presence of crystals in hard candies. Hard candies are non-chocolate sweets usually made of sucrose and glucose or of maltose syrup. They can also be made of alditols, used in sugar-free hard candies. In hard candies, carbohydrates or alditols are in amorphous state. Crystallisation in the glassy state of hard candies occurs as a result of a bad formulation, processing or storage and can be detrimental to the product quality. Differential scanning calorimetry was used to determine the glass transition temperature T_g and the amount of crystals. Polarising microscopy was used to show the undesirable presence of crystals in samples of hard candies. The carbohydrates composition of the samples was determined by HPLC and the moisture content in each sample was evaluated by Karl Fisher method.

Keywords: hard candy; the glass transition; crystallisation; differential scanning calorimetry; polarising microscopy

Hard candies are a liquid mixture of sucrose, fructose, glucose, glucose or maltose syrups, which are kept in amorphous or glassy state. Sucrose and glucose syrups are the basic components of the hard candies formulation. Fructose and partially glucose are the products of the decomposition of sucrose during the technological process. Glucose syrup is the product of acid-, and maltose syrup is the product of enzymic hydrolysis of starch. Both types of syrup are mixtures of glucose, lower or higher oligosaccharides, and other starch hydrolysis products based on glucosyl unit. Glucose is the prevailing component in glucose syrup, and maltose is the prevailing component in maltose syrup. Some types of hard candies are produced from reduced forms of the components mentioned above.

In appearance, hard candies are a solid, supercooled, noncrystalline liquid which finds itself below the melting or softening points (Anderson 1995). Hard candies are produced by evaporation of the solutions of sucrose and glucose or of maltose syrup under conditions where most of the water is removed. In the preparation of fruit candies, organic acids (citric, lactic, buffered lactic, malic and tartaric) are applied after evaporation. Organic acids are used to enhance fruit flavour and make hard candies tart. Depending on the technological conditions and ingredients, sucrose is partially hydrolysed to fructose and glucose.

In hard candies, sucrose hydrolysis may cause undesirable changes associated with an increase of their hygroscopicity. Sucrose hydrolysis also decreases the cooling rate during moulding which in turn affects sugars crystallisation and the hardness of the products (Shin *et al*. 1998). Crystallisation of amorphous sugars is probably the most typical crystallisation phenomenon in low moisture foods and is often detrimental to the food quality. Hard candies without crystals keep the desired shape and texture for a long time.

The glass transition temperature is an important physico-chemical property that affects the quality of hard candies. Hard candies bellow the glass transition temperature T_g and without crystals have

the shelf life desired. The value of T_g depends on the composition of glass, primarily on the average molecular weight (MW) of the system (Gabarra & Hartel 1996). Water and the average molecular weight of saccharides are therefore important parameters affecting T_g of hard candies.

The glassy state is a non-equilibrium state (Roos 1995). Although the driving force for crystallisation is extremely high, crystallisation of solutes is kinetically inhibited by the high viscosity of the system which is associated with the reduction of molecular mobility (Levine & Slade 1988; Gabarra & Hartel 1998).

Polarising microscopy and roentgen difractometry are very powerful techniques that allow the detection of crystals of sucrose or organic acids in hard candies. Many scientific papers describe studies of the glass transition temperature and melting conditions of crystals of different carbohydrates by differential scanning calorimetry (Roos 1993; Gabarra & Hartel 1996; Lupano 1997; Kedward *et al*. 2000).

The main objective of this study was to detect crystals in hard candies and to determine their glass transition temperature. The polarising microscopy was used to show the presence of sucrose crystals in hard candies, and the differential scanning calorimetry was used to determine their glass transition temperature.

MATERIALS AND METHODS

Set of symples. Commercial samples of hard candies utilised in this study were produced both by international and small producers in Europe and Asia and were bought in the retail in the year 2002. Wrapped samples were stored at 20°C and 40% relative humidity for one month.

Chemical analysis. The moisture content in each sample was evaluated by Karl Fisher method (Karl Fisher titrator AF8 Orion).

HPLC. Sugar concentration in hard candies was measured by HPLC. The samples were dissolved in distilled water to form 5% solution (w/v). The injected sample volume was 20 µl. The HPLC settings were as follows: pre-column 3.3 × 30 mm Separon SGX NH_2, column Tessek filled Separon SGX NH_2 particle size 5 µm, eluent acetonitrile: water 75:25, flow rate 1.0 ml/min, column temperature 30°C, detector RefractoMonitor IV. Data acquisition and peak processing were performed with DATA Apex software. The contents of higher oligosaccharides and other starch hydrolysis products w (%) (Table 1) were evaluated from the relation:

$$w = w_1 - w_2 - w_3 - w_4$$

where: w_1 – content of moisture (%)
w_2 – content of monosaccharides fructose and glucose (%)
w_3 – content of disaccharides sucrose and maltose (%)
w_4 – content of other ingredients (%)

Polarising microscopy. Representative samples of sucrose and citric acid crystals and samples of candies were studied by polarising microscopy (optical microscope Jenapol-Carl Zeiss Jena, cross nicols, scanning by digital colour Hitachi HV – C20M [3 CCD elements] evaluation by program LUCIA 4.21). A thin layer of each sample was measured directly on a glass microscope slide without a glass cover slip. The scale of crystals was determined according to Bartuška (1987) as shown in Figure 1.

Differential Scanning Calorimetry. DSC measurements were carried out using a SHIMADZU 50 and software TA 50. Approximately 10 µg of the sample was accurately weighed in aluminium pan and then heated from 20°C to 200°C. The heating rate was 10°C/min. The content of sucrose crystals in each sample was determined on the basis of the heat of fusion measured and the heat of fusion for crystalline sucrose.

RESULTS AND DISCUSSION

The contents of carbohydrates fructose, glucose, sucrose, maltose and lactose together with moisture for each sample of hard candies are presented in Table 1. It is evident that the samples with numbers from 20 to 24 had maltose syrup in the formulation. The sample No. 25 was a sugar-free hard candy with maltitol syrup and lactitol in the formulation. The remaining samples were produced from glucose syrup. The content of water that is the main plastificator in hard candies varied from 2.1% to 5.1%. The content of fructose, that is an indicator of the degree of sucrose hydrolysis, varied from 0.2% to 8.55%.

It can be seen from Table 2 that polarising microscopy showed the presence of sucrose crystals in all samples with the exception of the sample No. 23. The samples No. 1, 2, 5, and 13 had a greater amount of sucrose in crystalline phase (Figures 2 and 4) as

Table 1. The composition of samples

Sample No.	Content (%)						
	Moisture	Fructose	Glucose	Sucrose	Maltose	Lactose	*w*
1	3.6	2.31	7.12	56.51	3.44		26.02
2	3.6	4.06	4.58	87.74	–		–
3	3.0	5.69	9.69	34.65	4.69		41.28
4	3.5	0.52	6.26	48.17	4.43		36.13
5	3.6	0.95	7.00	42.31	4.54	0.19	40.41
6	2.3	3.28	11.66	40.64	6.33		34.78
7	3.4	1.33	6.30	54.35	4.10		29.52
8	2.1	1.70	8.46	40.83	4.17		41.74
9	3.7	1.68	8.71	50.18	5.79		28.94
10	3.5	1.30	6.78	61.22	3.50		22.71
11	2.2	2.95	11.06	47.07	4.78		30.93
12	3.4	0.17	1.77	52.50	4.91	2.59	33.65
13	4.9	8.55	12.44	59.50	0.70		12.90
14	2.1	1.11	9.95	42.24	9.78		33.82
15	4.4	3.05	8.46	39.91	4.64		38.54
16	4.2	2.02	5.58	43.05	3.60		40.55
17	4.7	2.48	10.68	31.70	4.56		44.89
18	3.9	1.40	6.74	52.41	4.73		29.81
19	2.7	1.03	4.99	60.22	5.76		24.29
20	4.0	0.24	1.05	56.69	15.36		21.66
21	3.9	0.22	1.08	53.90	20.12		19.78
22	3.1	2.07	4.57	49.65	13.06		26.55
23	2.5	0.39	3.73	43.36	21.27		27.75
24	5.1	1.49	2.93	32.01	13.87		43.60
			glucitol		maltitol	lactitol	
25	3.9	0.00	1.84	0.00	33.15	32.09	
26 (sucrose)	–	–	–	100	–		
min	2.1	0.2	1.1	31.7	0.7		
max	5.10	8.55	12.44	87.74	33.15		

proved by differential scanning calorimetry in the case of the sample No. 2 and 13.

The strongly crystallised candies can behave irregularly and differential scanning calorimetry is not able to determine any particular endothermic transition peak, and therefore the detection of crystals is difficult. The decomposition of the sample is shifted to lower or higher temperature (e.g. sample No. 5). Furthermore, the small portion of the sample (weight of 10 mg) need not be representative of the measured matrix. A discrepancy between the conclusions of polarising microscopy and any further technique can consequently arise (e.g. samples No. 1, 5, 16, and 24).

Table 2. Glass transition and crystals

Sample No.	T_g (°C)		Content of crystalline sucrose (%)	T_m (°C)	Presence of crystals
	onset	endset			
1	22.4	39.2	–	$\text{decomposition}_{150°C}$	strong
2	28.0	58.6	65.80	168.2	strong
3	39.7	52.15	0.40	184.0	weak
4	36.6	62.3	1.20	197.3	medium
5	24.8	42.0	–	$\text{decomposition}_{200°C}$	strong
6	47.4	59.9	0.60	187.6	weak
7	50.8	62.6	1.50	195	medium
8	41.6	54.5	1.50	176	medium
9	32.0	46.5	1.15	183	medium
10	44.7	59.3	–	$\text{decomposition}_{150°C}$	weak
11	52.8	65.7	–	$\text{decomposition}_{150°C}$	medium
12	51.7	63.8	1.80	165	weak
13	26.8	39	19.80	152	strong
14	49.7	65.4	–	$\text{decomposition}_{150°C}$	weak
15	–	–	–	$\text{decomposition}_{150°C}$	medium
16	38.9	53.9	–	–	medium
17	38.2	53.7	–	$\text{decomposition}_{150°C}$	medium
18	39.9	61.6	–	$\text{decomposition}_{150°C}$	medium
19	51.2	67.8	–	$\text{decomposition}_{150°C}$	weak
20	30.1	55.2	3.30	189.6	medium
21	32.0	61.9	1.00	172.7	medium
22	46.6	57.1	–	$\text{decomposition}_{180°C}$	weak
23	53.2	66.2	0.2	184	no
24	–	–	–	–	medium
25	35.5	52.8	1.40	187	weak
26	–-	–	100	188.7	crystallised
min	22.4	39		152	
max	53.2	67.8		197.3	

T_g did not occurred

Because the glass transition occurs over a temperature range, the onset and the endset of transition of the whole collection of hard candies were determined. The onset of the glass transition temperature ranged from 22.4°C to 53.2°C, and the endset temperatures from 39°C to 67.8°C. The onset and the endset temperatures of the glass transition T_g appear to be shifted to lower values with the increasing crystals content. With the increasing moisture content, the crystal content increases and the glass transition T_g decreases (Table 2, Figure 2). Contrary to this, the glass transition T_g is shifted to higher values with the increasing content of higher saccharides (Figure 3).

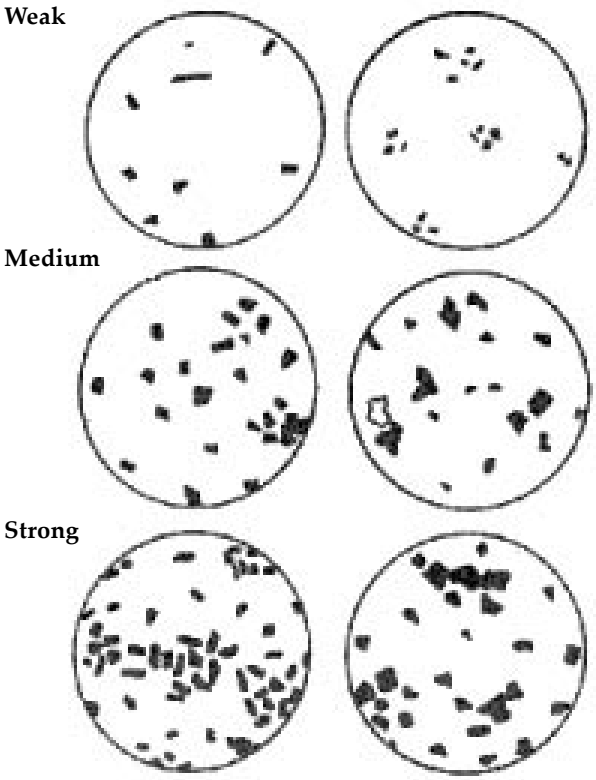


Figure 1. The scale of crystal content

There is a problem of the preparation of a representative material for the differential scanning calorimetry. In the case of polarising microscopy, the procedure of the sample preparation is rather more feasible. As shown in Figure 4, the sample No. 2 was extensively crystallised and the content of crystalline sucrose was very high (65.8%). An isolated crystal in glassy sample No. 6 is shown in Figure 5. Such crystals can occur as a result of a bad processing. A strongly crystallised upper layer is shown in Figure 6. Such deterioration of hard candies can be caused by bad storage conditions.

Table 3. The melting temperatute (T_m) and the heat of fusion (H_m) of sucrose according to the literature

	T_{m1}	T_{m2}	T_{m3}	H_{m1} (J/g)	H_{m2} (J/g)
Sucrose	173 (190)	160 (185)	192	118	120

1 – Roos (1993); 2 – Raemy *et al*. (1983); 3 – Slade and Levine (1991)

The sample No. 26 was pure crystalline sucrose used as a comparative sample. The melting temperature (T_m) of sucrose from literature varies from 160°C to192°C (Table 3). Under conditions described, the melting temperature of the sucrose sample was 188.7°C with the onset of melting at 165°C and endset at 197°C. The heat of fusion was 135.7 J/g. The T_m of samples ranged from 152°C to 197°C but some of them decomposed before melting. The decomposition was manifested on thermograms by a wide (decomposition) peak. The results of quantification of sucrose crystals by differential scanning calorimetry and by polarising microscopy are presented in Table 2 with the exception of the samples that were decomposed before melting and the determination of the content of crystals by DSC was thus impossible. It can be seen that both methods, i.e. polarising microscopy and differential scanning calorimetry, provided comparable results.

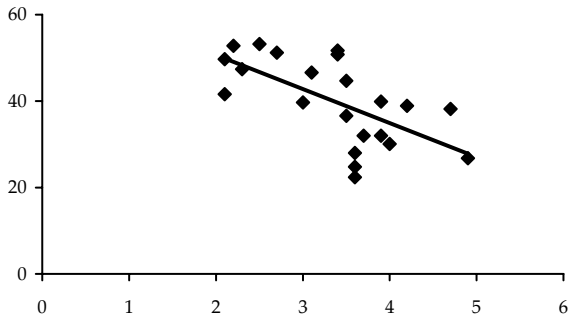


Figure 2. Relation between T_g and moisture

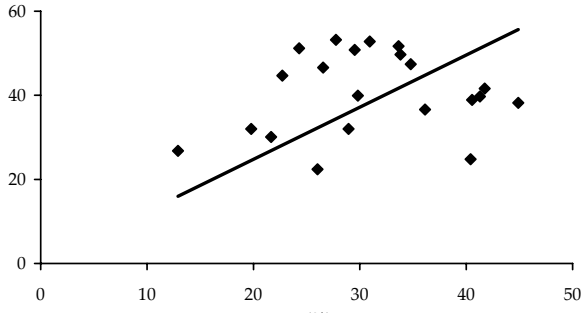


Figure 3. Relation between T_g and higher oligosaccharides and other starch hydrolysis products

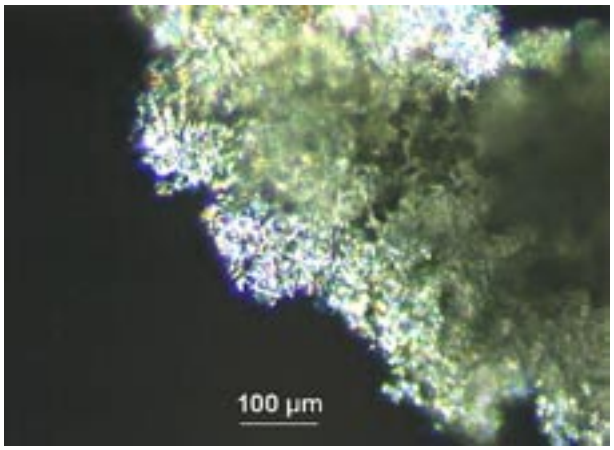


Figure 4. Strong crystallised sample No. 2

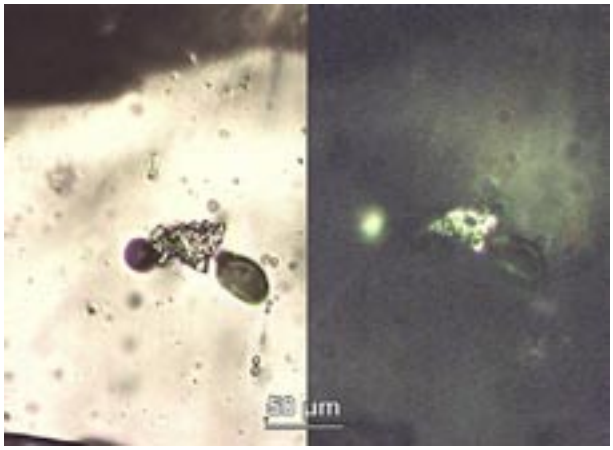
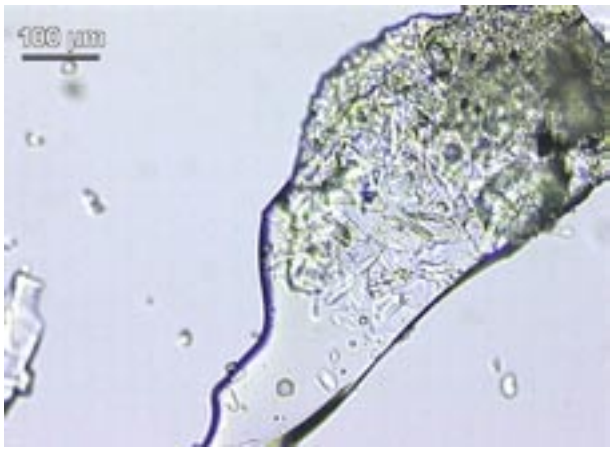


Figure 5. Isolated crystal in glassy hard candy in polarised light (left) and in polarised light with cross nicols (right) in sample No. 6



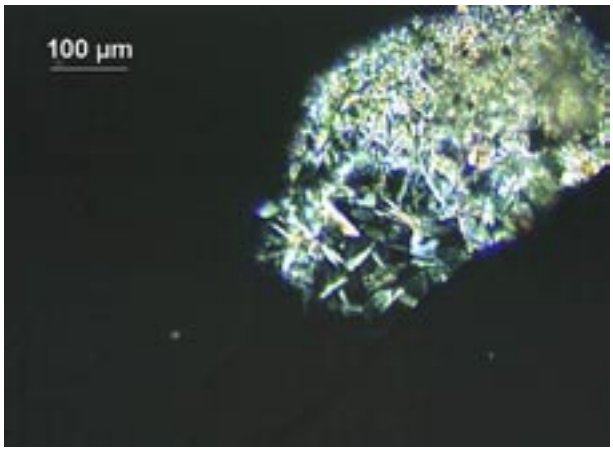


Figure 6. The deteriorated upper layer in polarised light and in polarised light with cross nicols – sample No. 13

Conclusion

This study showed that the moisture of hard candies was inversely correlated with their glass transition temperature. The higher their moisture content, the lower their glass transition temperature. The storage at a temperature above the glass transition temperature can cause crystallisation of glassy hard candies.

Polarising microscopy and differential scanning calorimetry are powerful techniques that help to follow and predict the shelf life of the product. Polarising microscopy allows the detection of the contents of sucrose crystals or of organic acids in hard candies. Differential scanning calorimetry is a useful technique in the detection of phase transitions, melting, and crystallisation or the glass transition temperature.

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References

Anderson L.J. (1995): Hard candy, formulations, variations and effects. Manuf. Conf., **75**: 33–36.

Bartuška M. (1987): Technická mineralogie. Skripta. VŠCHT, Praha.

Gabarra P., Hartel R.W. (1996): The influence of corn (glucose) syrup oligosaccharides on transition of amorphous sucrose. In: Int. Workshop Industrial Crystallization, Sept. 12–13, Bremen: 34–41.

Gabarra P., Hartel R.W. (1998): Corn syrup solids and their saccharide fractions affect crystallization of amorphous sucrose. J. Food Sci., **63**: 523–528.

Kedward C.J., MacNaughtan W., Mitchell J. R. (2000): Isothermal and non-isothermal crystallization in amorphous sucrose and lactose at low moisture contents. Carbohydr. Res., **329**: 423–430.

Levine H., Slade L. (1988): Collapse phenomena – A unifying concept for interpreting the behaviour of low moisture foods.In: Blandshard J.M.V., Mitchell J.R. (eds): Food Structure – Its Creation and Evaluation. Butterworths, London: 149–180.

Lupano C.E. (1997): DSC study of honey granulation stored at various temperatures. Food Res. Int., **30**: 683–688.

Raemy A., Schweitzer T. (1983): Thermal behaviour of carbohydrates studied by heat flow calorimetry. J. Thermal. Anal., **28**: 95–108.

Roos Y. (1993): Melting and the glass transition of low molecular weight carbohydrates. Carbohydr. Res., **238**: 39–48.

Roos Y.H. (1995): Phase Transition in Foods. Academic Press, San Diego.

Shin K.D., Lim S.T., Kim H.I. (1998): Effect of organic acids on the sugar composition of sucrose candies. Food Sci. Biotechnol., **7**: 100–106.

Slade L., Levine H. (1991): Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. Crit. Rev. Food Sci. Nutr., **30**: 115–360

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Souhrn

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Sledovali jsme skelný stav kandytů a identifikaci krystalů v kandytech. Kandyty jsou nečokoládové cukrovinky obvykle vyráběné ze sacharosy a škrobového nebo maltosového sirupu. Mohou se vyrábět i z cukerných alkoholů – alditolů (cukrovinky bez cukru). Cukry nebo cukerné alkoholy se v kandytech vyskytují v amorfním (sklovitém) stavu. Krystalizace sklovitých cukrovinek nastává jako výsledek špatné receptury, technologie nebo skladování a může výrazně poškodit kvalitu výrobků. Pro stanovení teploty skelného přechodu T_g a obsahu krystalů byla použita diferenciální skenovací kalorimetrie. Pomocí polarizační mikroskopie byl studován výskyt nežádoucích krystalů ve vzorcích kandytů. Byl proveden základní rozbor, tj. stanovení obsahu cukrů pomocí HPLC a stanovení obsahu vody titračně podle K. Fishera.

Klíčová slova: kandyty; skelný přechod; krystalizace; diferenciální skenovací kalorimetrie; polarizační mikroskopie

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