THE UNIVERSITY OF HULL

PREPARATION AND APPLICATIONS IN CONFECTIONERY OF CO-CRYSTALLINE SUGAR PRODUCTS

AND

A NOVEL HYDRATED FORM OF SUCROSE

being a Thesis submitted for the degree of

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by

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ABSTRACT

The formation of the solid crystalline phase of sugars plays an important role in many food products. The conventional crystallisation of sucrose gives solid, dense cubic crystals that have a limited surface area. On the other hand, co-crystallisation of sucrose is a process where a second ingredient is added to a supersaturated sucrose solution before crystallisation. The crystals obtained reveal a sponge-like appearance with considerable void space and interstices with the additive ingredient located in these interstices. The crystalline sugar products are said to be dry, granular, free-flowing and readily dispersible in water. It was shown that the co-crystallisation process improves the properties of a product such as its solubility, wettability and emulsification.

Even though a number of patents have been reported on the subject, little research works have been published. In particular, little information was available on the thermal properties of the materials formed and the crystalline characteristics of the agglomerate matrix.

In a preliminary work, the co-crystallisation of sucrose with honey was investigated. The Differential Scanning Calorimetry (DSC) and X-ray analyses showed that neither glucose nor fructose crystallised during the process. Nevertheless, glucose crystallised in the monohydrate form upon storage when a granulated honey was used.

In addition, different types of glucose were co-crystallised with sucrose in the proportions glucose-sucrose 10/90, 15/85 and 20/80. The DSC analysis showed varying crystallisation behaviour depending on the type of glucose used. The co-crystallisation of glucose with sucrose was extended to the proportions 85/15, 90/10 and 95/5. The process was adapted to glucose as main ingredient.

During the characterisation of the co-crystalline materials by DSC, an extra peak around 150°C was observed that could not be assigned to the second ingredient added or to a new crystalline phase formed by the constituents of the materials. The study of different sources of sucrose showed different behaviours by DSC analysis concerning this first melting peak. It was found that the purest sugar in terms of mineral salt content gave the highest intensity for this peak at 150°C. Further work under specific conditions of temperature and relative humidity permitted to isolate this phase believed to be due to a hydrated form of sucrose.

Finally, the process of co-crystallisation of glucose with sucrose was scaled up to 5kg. The DSC traces showed that the ingredient present in minority did not crystallise during the process and remained in the amorphous form even after several months of storage. The materials thus prepared were used in confectionery applications. A co-crystalline material containing 10% of glucose was tested in chocolate but proved to thicken it up. This result was believed to be due to the porosity of the co-crystalline product. As a consequence, its potential for fat retention was studied. The co-crystalline material was found to reduce the migration of hazelnut oil in a dark chocolate coating. Furthermore, pressed sweets were prepared with co-crystalline materials containing 10 and 90% of glucose respectively. They showed good tabletting properties even without the use of binding agent. The tablets prepared had a crushing strength similar to superior to those prepared with a granulated powder. They also showed good flavour retention.

ABBREVIATIONS

AG	Anhydrous Glucose
BPE	Boiling Point Elevation
DE	Dextrose Equivalent
DMF	Dimethyl Formamide
DMSO	Dimethylsulphoxide
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
F	Fructose
FC	Fisher Chemicals
FCMP	Full Cream Milk Powder
G	Glucose
GC	Gas Chromatography
GM	Glucose Monohydrate
HDPE	High Density Polyethylene
HPLC	High Performance Liquid Chromatography
HSM	Hot Stage Microscopy
LDPE	Low Density Polyethylene
NMR	Nuclear Magnetic Resonance
PID	Proportional Integral Derivative
R	Resistance
RH	Relative Humidity
RPM	Rotation Per Minute
SEM	Scanning Electron Microscopy

SMP	Skimmed Milk Powder
SP	Silver Spoon
SPME	Solid Phase Micro Extraction
SS	Coefficient of supersaturation
SW	Concentration in the solution
SWsat	Concentration of the supersaturated solution
TAG	Triacylglycerol
T&L	Tate and Lyle
Tg	Glass transition temperature
W	Water

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CHAPTER I

SUCROSE: PRODUCTION AND PROPERTIES

Sugar is one of the oldest foods. This natural product appears throughout the history and literature of the civilised world. Today it is one of the most commonly used ingredients in the food industry. It is produced from sugar cane or sugar beet in almost every country.[1]

Sugar is a major commodity in world trade. Over 100 million tons of sugar have been produced world wide annually in recent years. Approximately a similar amount is consumed. Sugar can be produced in the temperate zones as well as in tropic and subtropics. Sugar beet accounts for most of the sugar produced and consumed in Europe.[2]

Thus, sucrose as a constituent of the human diet is quite unique. On the one hand, it is commercially produced in a chemically pure form and, on the other hand, it constitutes a substantial part of the human caloric intake.[3]

1.1. Process sugar from sugar cane.[4]

1.1.1. Raw sugar processing

After the cane is delivered, excessive soil and rocks are removed. The cane is crushed and hot water is sprayed onto the crushed cane to aid the extraction of sugar. The juice obtained is limed, heated and sent to the clarifiers. The clarified juice is sent to evaporators; it contains about 85% of water and is concentrated by heating in vacuum evaporators to remove about two-thirds of the water. The syrup leaving the last vacuum boiler contains about 35% of water. The syrup is further concentrated in the crystalliser vacuum pans until saturated with sugar. Seeds are added to serve as nuclei. When sucrose concentration reaches the desired level, the dense mixture of syrup and sugar crystals, called massecuite, is allowed to flow into the centrifugals where the very thick syrup known as molasses is separated from the raw sugar by centrifugal filtration. Raw sugar contains generally 96 to 99% of sucrose.[5-8]

1.1.2. Cane sugar refining

The raw sugar is submitted to five basic operations during refining:

- Centrifugation
- Filtration
- Decolourisation
- Evaporation
- Crystallisation.

The first step separates the surface molasses film from the relatively pure raw crystalline sugar. This is accomplished by mingling hot, saturated syrup with raw sugar followed by centrifugation. Washed raw sugar is dissolved in high purity sweet-water to a high-density sugar liquor. The liquor is treated with lime and carbon dioxide. This liquor is clarified and passed through a filtration apparatus that removes the colloidal particles.

Decolourisation is generally accomplished by passing the sugar liquor through a decolourising column containing a charcoal like material. It is then evaporated through a multiple effect evaporator. In the vacuum pan, the evaporation process continues until seeding procedures using tiny crystals shock the supersaturated solution into producing an initial crop of crystals. The mixture is, once again, centrifuged. The damp crystals are dried through heated air in a granulator before screening and packaging.

1.2. Sugar beet processing[4]

The complete sugar beet processing operation involves a number of unit operations including:

- Diffusion
- Carbonation
- Evaporation
- Crystallisation.

The sugar beet is washed and sliced. The sliced sugar beet is transported in a direction against the flow of hot water extractant. Juice from the diffuser is purified with lime and carbon dioxide. The heated juice is sent to a clarifier. The clarified juice is concentrated from 13% to 60-65% in evaporators. Thick juice from the evaporators is further concentrated and the sugar is crystallised. Crystallised sugar is separated from the massecuite mother liquor by centrifugation. The white sugar is dried in a granulator to a moisture content of about 0.02%. The white refined sugar produced is 99.96% pure.

Sugar refining today has many additional means of improving and accelerating the refining processes[9-13] that are not detailed in this work.

1.3. Sugar products[14,15]

A wide variety of crystalline forms of sucrose is available from the refiners, with differences based mainly on particle size. These range from fondant icing sugar up to large-particle-size granulated sugar. Liquid sugar is also available for products that do not require a crystalline form. Two other categories of sugar products are brown sugar and speciality products such as sugar products specially made for direct compaction or fondant-quality sugar that can be extruded.

1.4. Structure of sucrose in the crystal and in solution

1.4.1. Nomenclature

Most monosaccharides exist in the form of heterocyclic rings i.e. cyclic hemiacetals, composing either five membered furanoses or six membered pyranoses. The centre of chirality generated by hemiacetal ring closure is called an anomeric centre which is the only carbon bound to two oxygen atoms. It is labelled C_1 and the others are numbered sequencially around the ring. The two stereoisomers are referred as anomers, designated α and β according to the configurational relationship between the anomeric centre and a specified anomeric reference atom. The D and L designation of the configuration refers to the position of the hydroxyl group on the asymmetric carbon farthest from the C_1. The official name of sucrose is β-D-fructopyranosyl-α-D-glucopyranoside.

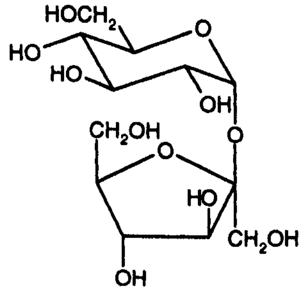

Figure 1.1: Sucrose molecule

A disaccharide is a compound in which two monosaccharide units are joined by a glycosidic linkage. When there is no hemiacetal group free, the resulting disaccharide is known as a non-reducing sugar. This is the case for sucrose.

1.4.2. Structure of sucrose in the crystal

1.4.2.1. Conformation of sucrose[16]

The common sucrose formula does not give any three dimensional information about the actual predominating conformation, nor does it give any hint of the selectivity of deprotonation which is to be expected. A more realistic picture is obtained from X-ray analysis of the solid state conformation showing the glucose and fructose moiety fixed in their relative orientation by two strong interesidue hydrogen bonds between 5-Og...HO-6f and 2-Og...HO-1f of 1.89 and 1.85 Å length, respectively.

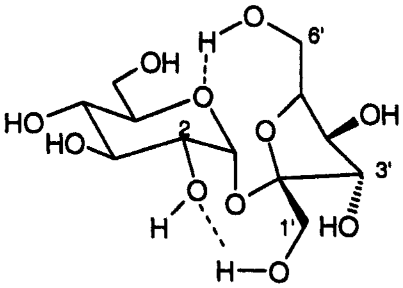

Figure 1.2: Structure of sucrose in the crystal[16]

The crystals of sugar belong to the monoclinic system $P2_1$.[17] The unit cell contains two molecules (Figure 1.3) the dimensions of which are as follow[18]:

a = 10.868(2) Å b = 8.710(1) Å c = 7.761(1) Å β = 102.97(1)°

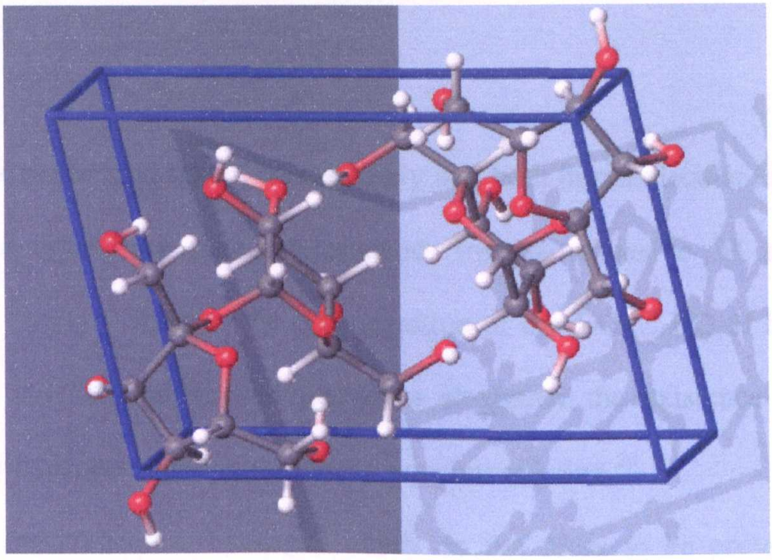

Figure 1.3: Sucrose crystalline cell[19]

1.4.2.2. Packing features of crystalline sucrose[17]

In the molecular arrangement found in the crystal structure of sucrose, the packing is highly dense, due to each molecule being surrounded by 12 nearest neighbours; this is in agreement with the high density (1.59) of the crystals.

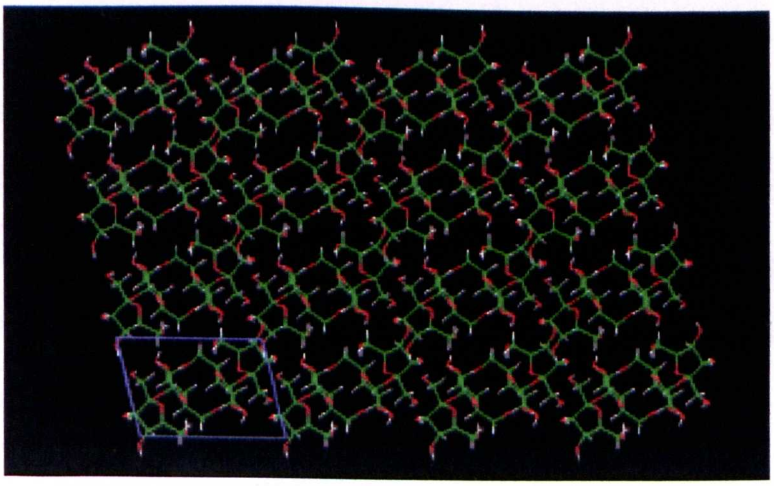

Figure 1.4: Packing of sucrose molecules[19]

1.4.3. Structure of sucrose in solution[16]

In solution, particularly in water, it is unlikely that both intramolecular hydrogen bonds present in the crystalline state are retained. Indeed, extensive ^{1}H and ^{13}C NMR investigations strongly attest to the disintegration of the 5-Og...HO-6f hydrogen bond by solvation, a NMR study even questions altogether the existence of any stable intramolecular hydrogen bond in sucrose in aqueous solution.[20]

Even though intramolecular hydrogen bonds do not seem to be present in aqueous solution, two sucrose hydrates have been found by infra-red spectroscopy: sucrose penta and dihydrate. The two hydrates observed in aqueous solution were not found in the solid state.[21] Furthermore, molecular dynamic simulation showed the occurrence of a water-mediated hydrogen bond bridge between the glucose and fructose moiety in highly concentrated solutions.[22,23]

1.5. Amorphous sucrose[24]

The difference between materials in the amorphous and liquid forms is the departure from equilibrium. Amorphous solids have very long relaxation times and may remain almost indefinitely in a metastable state. Amorphous is not synonymous with absence of order. There is always a certain structure which depends on the way a glassy or an amorphous solid is prepared (Figure 1.5). Amorphous sugar can result from dry-milling, quenching of a melt, rapid drying of solutions (spay-drying) or freeze drying of aqueous solutions. The glass transition of amorphous sucrose is reported in the literature to range between 50 to 70°C.[25] Urbani *et al.* reported the different values found in the literature. By using Dynamic Differential Scanning Calorimetry they measured the Tg to be 68.5 ± 0.5°C. Water content and water activity together with temperature are the determining factors for the mobility and reorganisation of sucrose molecules in the amorphous matter. The stability of amorphous sugar in foods is of practical and economical importance. It affects quality attributes such as texture, aroma retention and shelf-life. Van Scoik *et al.*[26] have studied the phase transformation of amorphous to crystalline sucrose and the effect of impurities.

The glass transition temperature of amorphous sugar was found to depend on moisture content and method of preparation.[27,28] It decreases on increasing water content. A small amount of moisture (1%) provokes a decrease of about 20°C of the Tg value of a freeze-dried sample.[29]

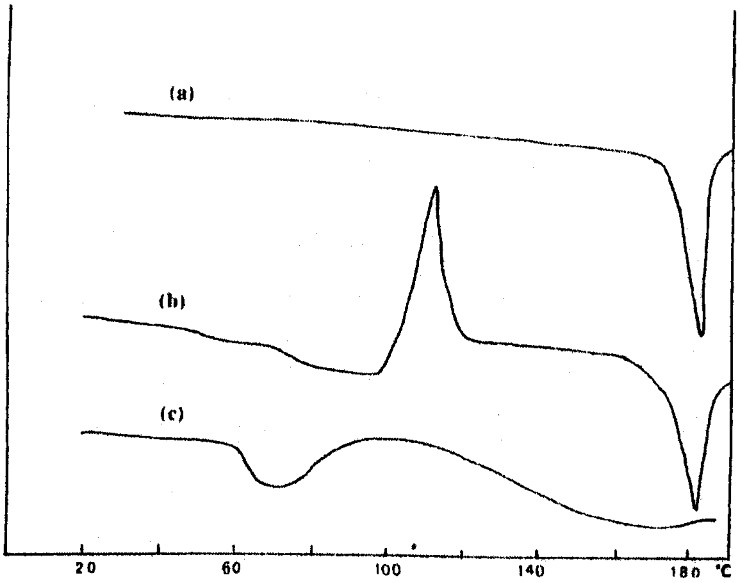

Figure 1.5: Differential thermograms of a) crystalline, b) lyophilized and c) vitreous sucrose[24]

1.6. Sucrose solubility

The definition of "sucrose solubility" is the concentration of sucrose in a saturated solution which is in equilibrium with sucrose in the solid state. The solubility of sucrose in water is of fundamental importance in defining the supersaturation or driving force of sucrose crystal growth.

A molecule of sucrose has eight hydroxyl groups, three hydrophilic oxygen atoms and 14 hydrogen atoms. This enables the formation of hydrogen bonds with water molecules, hydration of sucrose molecules and therefore easy dissolution of sucrose in water. In non-aqueous solvents, sucrose solubility is significantly lower than in water and sucrose does not dissolve in non-polar solvents.

1.6.1. Sucrose solubility in water[30]

The solubility of sucrose increases significantly with temperature. This dependence is called the solubility curve. Table 1.1 gives the values for the solubility of sucrose at various temperatures.

Temperature (°C)	g of sucrose per g of water	Temperature (°C)	g of sucrose per g of water
-10	1.7615	65	3.0598
-5	1.7837	70	3.2515
0	1.8127	75	3.4616
5	1.8489	80	3.6901
10	1.8926	85	3.9368
15	1.9443	90	4.2003
20	2.0047	95	4.4775
25	2.0741	100	4.7637
30	2.1535	105	5.0335
35	2.2435	110	5.4499
40	2.3450	115	5.9347
45	2.4589	120	6.5062
50	2.5863	125	7.1895
55	2.7282	130	8.0211
60	2.8857		

Table 1.1: Solubility of sucrose in water[30]

1.6.2. Phase diagram for the system sucrose-water

Sucrose solubility in water is graphically expressed in Figure 1.6. The curves of sucrose solubility and ice solidification which intersect at the eutectic point are shown. Above these curves, the solubility curve begins at the point of sucrose melting (186°C), separates undersaturated sucrose solutions from the two phases system saturated solution-solid sucrose and finishes at the eutectic point (-13.9°C). The solidification curve illustrates the equilibrium between the undersaturated solution and solid phase of the solvent, i.e. ice. Under the temperature of the eutectic point, ice continues to form whereas sucrose concentrates in concentrated amorphous solutions.

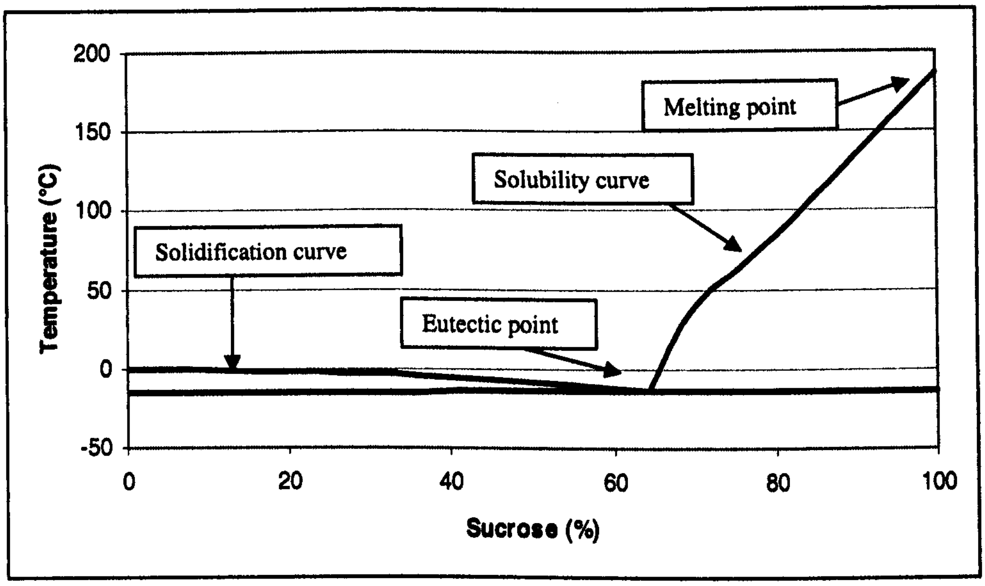

Figure 1.6: Sucrose-water phase diagram[30]

Few studies of multicomponent solvent mixtures of sucrose have been reported.[31-33] Peres *et al.* give the solubility of sucrose in water-ethanol, water-methanol and ethanol-methanol at 25, 40 and 60°C.[34]

1.6.3. Supersaturated solutions[35]

A solution that contains more sugar molecules than is thermodynamically allowed is said to be supersaturated. Several methods are available for generating a supersaturated solution. The first is by cooling an undersaturated solution. If cooled far enough, the concentration of the solution will pass over the solubility line and the solution will be supersaturated. This is shown by line AB on Figure 1.7. The degree of supersaturation depends on the initial concentration and the extent of cooling. Another means of generating supersaturation is by removing some of the water to increase the relative content of sugar molecules in solution. This is achieved by evaporation and is shown as line AC in Figure 1.7. This method is used by the sugar refiners for purifying sugar. A third method is to add a second solvent in which sugar is not soluble. Alcohols are convenient solvents for sugars due to their low solubility values. The solution mixture, following addition of a solvent, has a lower solubility for sugar than the initial solution. Thus the concentration even though diluted slightly by the solvent addition, becomes supersaturated with respect to the solvent mixture. This is shown in Figure 1.7 by the line AD in combination with the new solubility curve (dashed line).

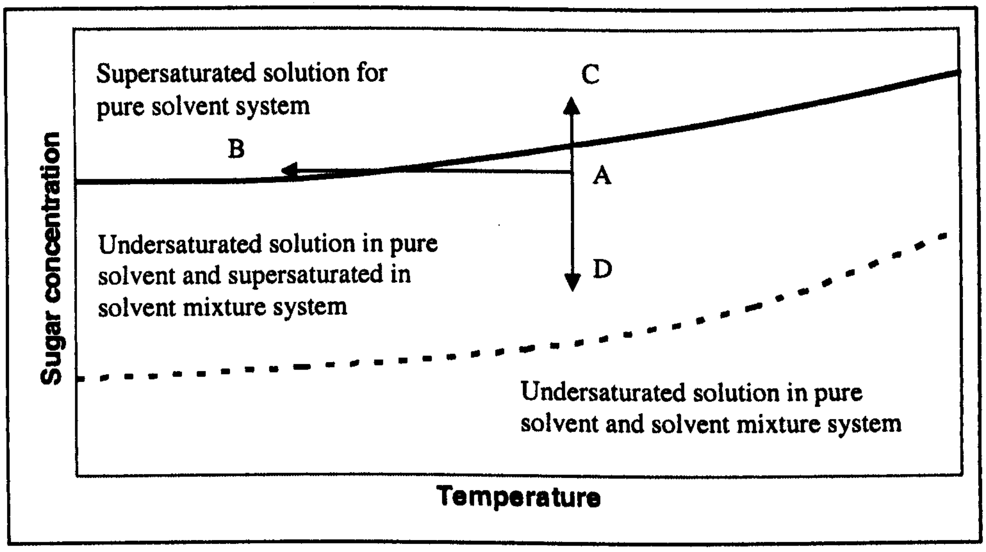

Figure 1.7: Formation of a supersaturated solution[35]

This supersaturated state may keep for quite a long time in the absence of a solid phase although it is a thermodynamically unstable state. It is caused by the increase in viscosity and limitation of movement of the molecules especially for the two first methods. The creation of a supersaturated solution is a condition for separating the solid phase from the solution. The amount of supersaturation can be expressed by means of the coefficient of supersaturation, SS, which expresses the ratio between a given sucrose concentration in the solution, SW (g sucrose per g water) and concentration of the saturated solution, SWsat, at the same temperature. Thus,

$$SS = SW/SWsat$$

1.6.4. Sucrose solubility in impure sugar solutions and impure solvents

The solubility concentration of a material may be dramatically changed by the presence of impurities. For sucrose, the presence of materials such as glucose syrup, invert sugar, glucose, gelatine, proteins and starches generally causes a decrease in the saturation concentration.[35] The solubility of glucose-sucrose mixtures is given by Horn as a function of temperature.[36] Figure 1.8 shows the amount of sucrose and glucose that will dissolve when one or the other is at saturation. Syrups on the left-hand portion of the curves are saturated with respect to sucrose. Those on the right are saturated with respect to glucose. The peak represents the concentration where the solution is saturated with respect to both sugars.

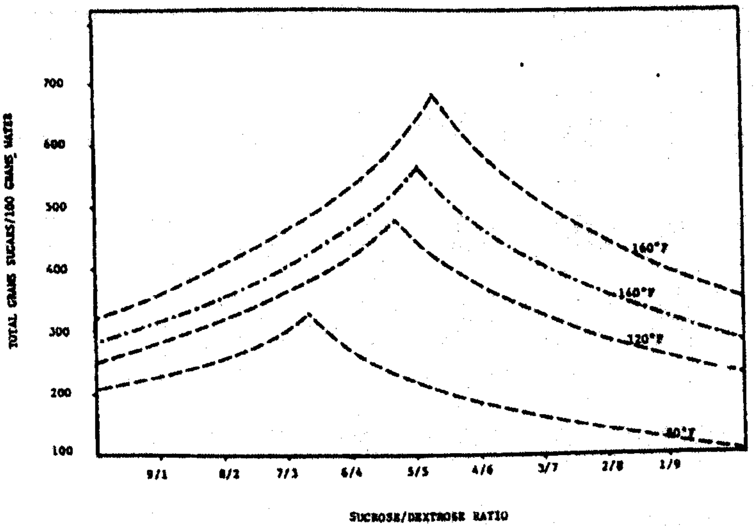

Figure 1.8: Solubility curves of sucrose-glucose mixtures[36]

The decrease in solubility of sucrose when some impurities are present might suggest that the sucrose would nucleate more readily in the presence of additives for a constant level of sucrose in solution since the supersaturations are higher under similar conditions. However, this is not the case since there is an inhibition effect on the formation of nuclei from these additives.

1.7. Metastability[35]

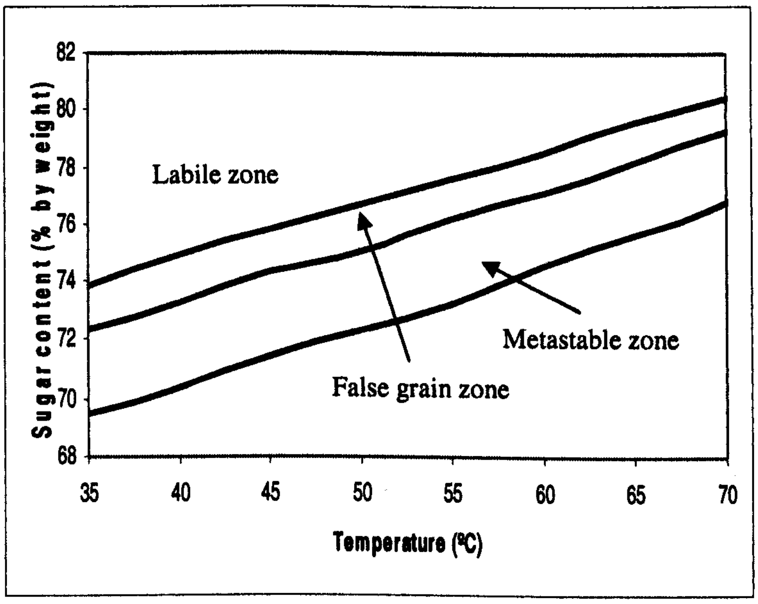

Figure 1.9: Metastable regions of sucrose[37]

When a supersaturated sugar solution is created, a driving force exists for the formation of the crystalline phase. However, even though a sugar solution is supersaturated, it generally will not crystallise until the driving force exceeds a critical value. This critical supersaturation is related to the energy requirements for the formation of the solid phase, or the energy barrier to nucleation. The region of concentration between the saturation concentration and the critical concentration is called the metastable region of supersaturation. This region varies with parameters such as temperature, agitation rate and level of impurities. Each of these parameters influences the energy barrier to the formation of the solid phase. Typical curves for sucrose are shown in Figure 1.9. This figure shows several curves that are related to the type of nucleation mechanisms that can occur.

The solubility curve, at higher supersaturation, represents the boundary at which spontaneous nucleation will occur: that is above this value of supersaturation, nuclei will form spontaneously by some heterogeneous mechanism. In a narrower region of supersaturation conditions at lower concentrations, nucleation will only occur when existing seed crystals are present. This is commonly called secondary or forced nucleation. At even lower supersaturations, nucleation will not occur under any conditions; however, existing crystals will still grow. The concentration boundaries for these regions are not really clearly defined and will vary with changes in parameters such as agitation rate and additives. For this reason, the values for the metastable range reported in the literature are quite variable. The curve for sucrose was developed for stagnant solutions. Under agitated conditions, the critical supersaturation for nucleation may be lowered.

1.8. Crystallisation

1.8.1. Morphology of a single crystal of sucrose[37,38]

Vavrinecz[39] described in detail that sucrose morphology can be considered as all the faces of the crystal which determine the sucrose external habit. Sucrose is characterised by 15 simple forms; the positions of the faces are shown in Figure 1.10a. The eight most important faces are shown in Figure 1.10b. The faces of the crystals are in general identified either by their Miller's indices or by conventional letters.

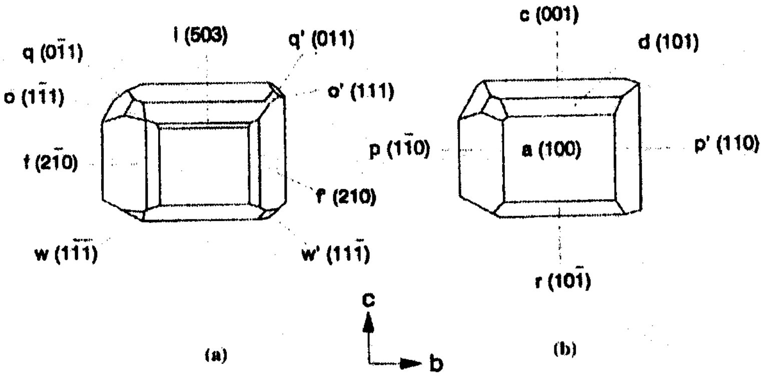

Figure 1.10: a) Sucrose crystal showing all the 15 forms. b) The eight most important faces. (The miller's indexes of the different faces are indicated in brackets)[38]

The relative development of the different faces depends upon the different growth rates and determines the exterior shape of the crystal. In particular, the faces which most rapidly form tend to disappear from the final morphology where in general, the eight faces mentioned above can be found. In pure solution, the faces of the right pole (+b) grow more rapidly than those of the left pole (-b). The presence of glucose and fructose has been reported to modify the usual sucrose crystal morphology to a D shape.[40] Raffinose is also known to adsorb on some faces of the crystal affecting the habitus of sucrose crystal.[41]

1.8.2. Nucleation[35]

Nucleation is the formation of a solid crystalline phase from a supersaturated sugar solution. Crystal nuclei are formed when sufficient energy is available for the formation of the solid phase from the solution structure at a given concentration and temperature.

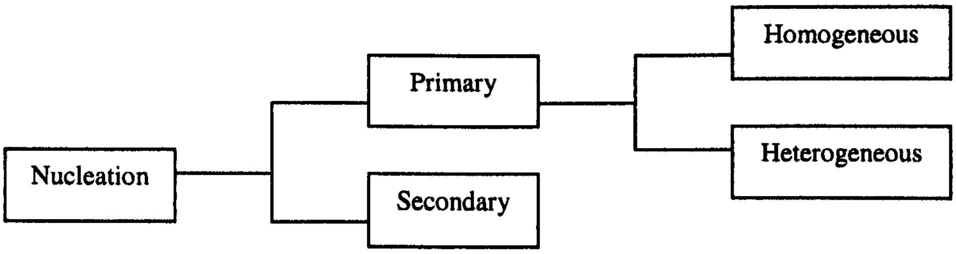

Figure 1.11: Classification of nucleation mechanisms[35]

A typical classification of crystal nucleation mechanisms is shown in Figure 1.11. Nucleation mechanisms may be divided into two broad categories. Primary nucleation mechanisms are those in which nuclei are formed in systems that do not contain crystalline centres of crystallising material. The primary nucleation processes require an energy barrier associated with the formation of a new nucleus to be overcome. This is the energy required to form the crystal surface and the crystal mass. The phenomenon of secondary nucleation is different in that the presence of an existing crystal surface is required for generation of nuclei. The rate of secondary nucleation was found to be linearly dependent upon the total surface area of the crystals present and to be self enhancing.[42]

Homogeneous nucleation is the classical process of partial formation described by a molecular accretion mechanism: that is, molecular collisions lead to the creation of clusters of molecules that become large enough to exceed the energy barrier to nucleation and become stable. Before reaching the critical radius of a nucleus, embryos are formed as hexamers.[43] Regular stacking of sucrose molecules around embryos takes place at the origin of the nuclei which are comprised of about 80-100 molecules. The rate of passing from embryo to nucleus is lower than that of embryo formation. It is possible that embryos exist in undersaturated solutions at the range of concentrations from 44% to 67% at 20°C.

The frequency of collision of these embryos leads to a probability of appearance of critical nuclei given by:

$$J = kT/h \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$$

The first term in this relation is a universal term. In the second term, the variation of entropy plays a major role. There is a need for a high ΔS^* for at least two reasons: the evolution from disorder to order on the one hand and the evacuation of hydration water on the other hand.

Nucleation by a strict homogeneous mechanism as described above rarely occurs in supersaturated sugar solution due to the presence of impurities that act as nucleation sites. Certain impurities, such as dirt or dust particles, rough or pitted container surfaces may catalyse the formation of the crystal nucleus and allow nucleation at much lower supersaturations than are required for homogeneous nucleation.

The studies of primary nucleation processes in sucrose have generally involved either determinations of the time required for the appearance of nuclei under certain conditions or the visual counting of the number of nuclei appearing after a certain period of time at supersaturated conditions. Nucleation experiments involving the formation of nuclei in small diameter droplets have allowed the observation of homogeneous nucleation of sucrose solution. It has been found[44,45] that homogeneous nucleation occurs at a supersaturated ratio in excess of 1.5 to 1.6. Under normal conditions, spontaneous nucleation of sucrose solution occurs at a supersaturated ratio of 1.2 to 1.3.

1.8.3. Growth[46]

Crystal growth theories tend to be categorised into two main groups. First are the adsorption layer theories, sometimes referred to as surface integration theories. They describe the incorporation of growth units into the crystal lattice.

Second, the mass transfer limiting theories account for the movement of molecules through the bulk of the solution to the crystals interface, where the incorporation into the crystal lattice is considered to occur instantaneously.

The first step is expressed by:

$$Vr = kr\,(C_1 - C_0)^2 \qquad \text{Equation 1}$$

where C_1 is the sucrose concentration in the vicinity of the crystal and C_0, the concentration of the solution (saturated) at the contact of the crystal. kr is the constant for the incorporation of molecules in the crystal.

The rate of the second step is described by Fick's first law:

$$Vd = kd\ (C - C_1)/d \qquad \text{Equation 2}$$

Where: Vd is the quantity of sugar which diffuses to the crystal per unit surface of crystal and unit of time; C and C_1 are, respectively, concentrations of the solution and of the thin layer around the crystal whose thickness is d; kd is the diffusion coefficient.

Combining Eq. 1 and Eq. 2 yields an expression for the overall rate of growth where the unknown concentration C_1 at a short distance from the crystal is eliminated:

$$V = kd/d\ (kd/2dkr + \Delta C - (kd/dkr(\Delta C\text{-}k1/4dkr))^{1/2}) \qquad \text{Equation 3}$$

where $\Delta C = C\text{-}C_0$

This equation is comparable to that proposed by Frank[47]. Other authors express Vr as Vr = kr (C_1-C_0) which yields a simpler relation for V:

$$V = (C\text{-}C_0)\ (d/kd + 1/kr) \qquad \text{Equation 4}$$

For temperatures above 45°C, kr is preponderant, so that 1/kr is negligible compared to 1/kd. Replacing the diffusion coefficient kd in Eq. 4 by the expression

$$kd = kT/6\Pi\eta r$$

established for dilute solutions leads to the classical relation:

$$V = kT\ C_0(\ \sigma - 1)^x/\ \eta^y \qquad \text{Equation 5}$$

where: T is temperature in K; η viscosity in mPa.s; C_0 the ratio sugar/water given in solubility tables; σ the saturation coefficient; and x and y are constants. Comparing the rates of growth obtained by application of Eq. 5 with experimental results permits the determination of the empirical parameters x and y in the following relation:

$$V = 10^{0.0183T} . C_0 (\sigma - 10)^{1.5} / \eta^{0.731} \qquad \text{Equation 6}$$

Experimental data obtained by Kukharenko[48] fit well with the rates calculated by use of Eq. 6. It may be noticed that $\eta^{0.731}$ is much lower than the viscosity of saturated sucrose solution. Such an empirical exponent used for viscosity as well as that of supersaturation questions the preponderance of diffusion based on Fick's law and Stockes-Einstein relations in the crystallisation process.

Significant effort has gone into quantifying the rate of sucrose crystal growth and to understanding the mechanisms that govern growth under a variety of conditions. The different results lead to the conclusion, clearly stated by Van Hook[49], that the mechanism of sucrose crystal growth is comprised of more than one step. Based on the relative activation energies and the influence of the agitation level, both mass transfer effects and the surface incorporation step must be accounted for in sucrose crystal growth. At elevated temperatures, mass transfer effects tend to dominate and this becomes the rate-limiting step for growth. However, below 40°C or near to this temperature, the surface incorporation step becomes more important and the effects of mass transfer on the overall crystal growth rate are reduced significantly.[50] The effect of impurities on growth rates has been studied and raffinose was found to reduce the growth rate. Furthermore, glucose and sodium carbonate were found to reduce both nucleation and growth rates with sodium carbonate having the stronger effect.[51]

1.8.4. Hydrates[52]

It is generally accepted that sucrose forms exclusively anhydrous crystals, however during the study of the sucrose-water phase diagram at a temperature range of -34°C to 0°C, this was found not to be the case and that there were some circumstances that resulted in the formation of sucrose hydrates. A sucrose hemipentahydrate $C_{12}H_{22}O_{11}$.

5/2 H_2O and a sucrose hemiheptahydrate $C_{12}H_{22}O_{11}$. 7/2 H_2O were isolated and characterised.

Both hydrates demonstrated specific powder X-ray diffraction patterns which were distinct from the anhydrous phase and which had melting points of 45.7 and 27.8°C respectively. Progressively decreasing the temperature was shown to result in an increasing complexity of the metastability characteristics of the system, especially on the approach to the ice eutectic where no less than eight solid phases seemed to be possible, in addition to the anhydrous phase. Unfortunately, these additional phases were not positively identified.

1.8.5. Crystallisation in thin film[53]

When considering crystallisation in thin films, the degree of supersaturation is a crucial factor that must be considered. Sugar technologists rarely refer to the supersaturation level above 1.3 when considering vacuum pan crystallisations.

Thin films of syrup exposed to an atmosphere of controlled humidity resulting in molecular evaporation may produce very high degrees of saturation where nucleation may be slow. When nucleation occurs the nuclei, produced at about 1.5 to 2.0 SS, are predominantly euhydral and can show some signs of internal disorder (Figure 1.12). At 2.0 to 3.0 SS, multicrystals known to crystallographers as spherulites, are observed (Figure 1.13). By 4.0 SS, all nuclei appear to be spherulitic. In the case of spherulites, the component crystals appear to radiate from a common origin, and each ray is a single crystal.

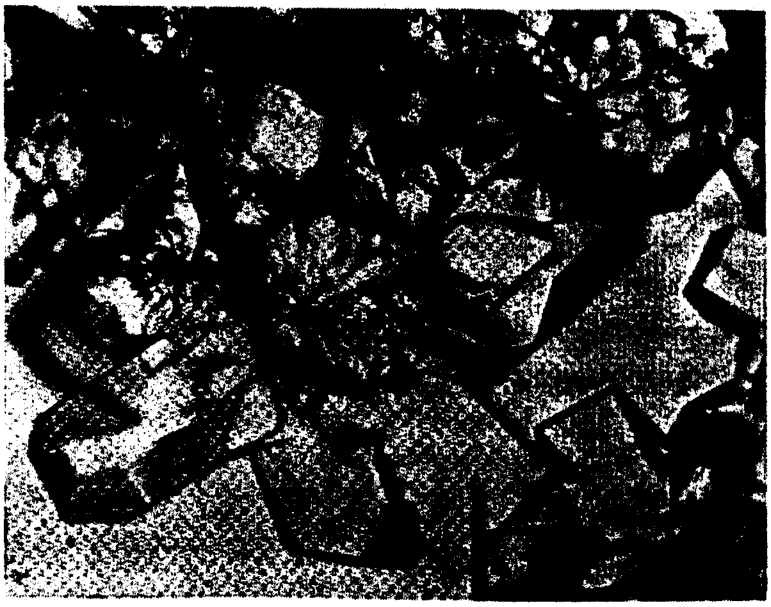

Figure 1.12: Euhydral growth[53]

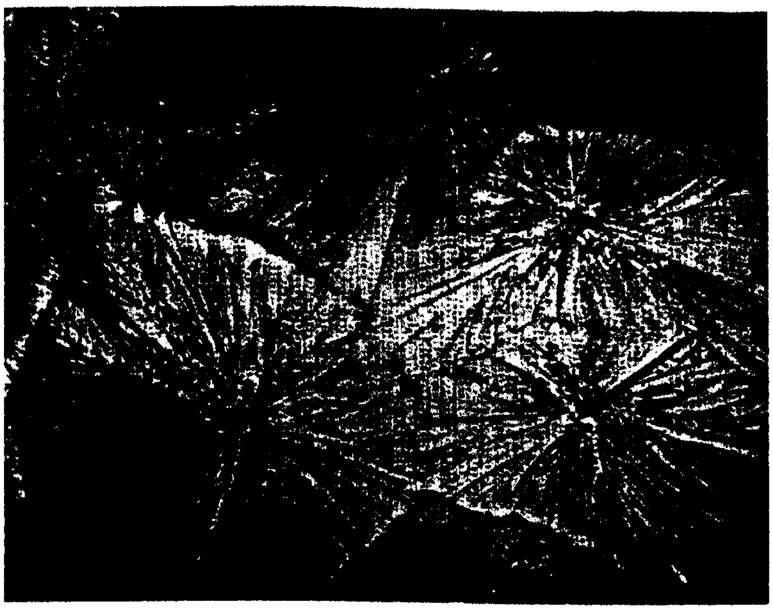

Figure 1.13: Spherulitic growth[53]

The crystallisation in thin film by seeding has been found[54] to induce a linear increase in crystal size. The crystal growth rate increases with increase in temperature in the range 25-30°C but no significant change in crystal growth is observed by increasing concentration from 70 to 76%.

1.8.6. Inclusions[38]

The internal characteristics of the crystal can be conditioned by the presence of impurities inside the crystal lattice. These impurities can be either coloured or colourless and they can have high or low molecular weights. Taking into account that the presence of such substances can be very important in relation to crystal quality and, in particular, colour and ash content, it is clear that such parameters have been extensively studied, often yielding conflicting results.

A number of researchers emphasise that certain compounds, which are coloured and have a high molecular weight, can be bonded to the sucrose molecules at the different crystal faces. On the contrary, other authors ascribe the major importance to the phenomenon of physical capture of mother liquor microdroplets or macrodroplets inside the crystal. The presence of such inclusions has been widely studied by Powers[55] using photography.

Recently, it was pointed out that the capture of mother liquor can be caused by particular growth kinetics conditions, which, by destabilising the crystal surface, can create hollows able to capture solution.[56] Taking into account that the various crystal faces have different growth rates it has been proposed that the most rapidly growing faces can include mother liquor more rapidly than the others independently of the crystals that originate from either beet or cane processing.

1.9. Chemical and physical properties

1.9.1. Chemical properties

All sugars are fairly reactive. However, with sucrose the main reactive site which is at the anomeric carbons of each of the D-glucose and D-fructose molecules is already taken up by forming the sucrose molecule. The two monosaccharides are therefore much more reactive than sucrose. In fact, they are termed reducing sugars because of their ability to act as weak reducing agents. In contrast, sucrose is a non-reducing sugar due to the acetal linkage at the anomeric centres of both glucose and fructose.

In acidic solutions, sucrose will invert or in other words, break down into its two component monosaccharides glucose and fructose.[57,58] This reaction is accelerated with increasing acidity and increasing temperature.

1.9.1.1. Inversion reaction

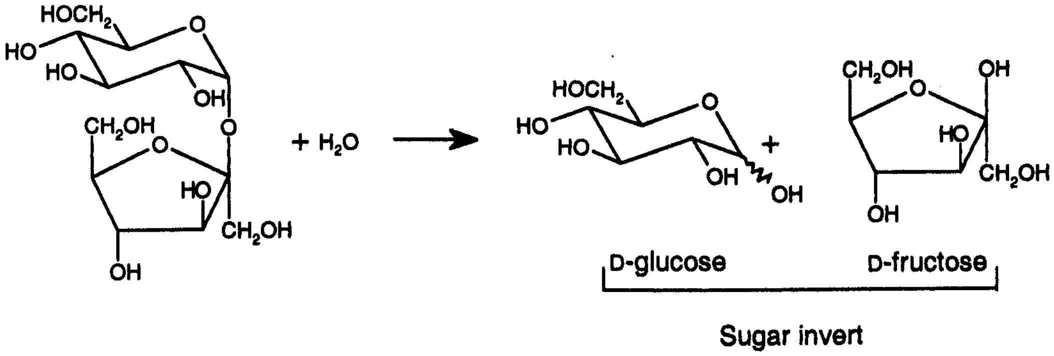

Figure 1.14: Inversion of sucrose

This is an irreversible hydrolysis reaction in which one sucrose molecule and one water molecule yield one molecule of fructose and one molecule of glucose. This reaction proceeds more quickly with temperature. Inversion of pure sucrose solutions proceeds nearly 5000 times faster at 90°C than at 20°C. In practical terms, this reaction takes place below pH 7 and proceeds more quickly as the pH decreases. This reaction can also proceed by biochemical catalysis with several enzymes[59,60] most notably those known as invertases.[61,62]

1.9.1.2. Thermal decomposition

Dry, crystalline sucrose is fairly stable up to its melting point (186-192°C).[27] Molten sucrose will decompose rapidly without loss in weight into D-glucose and D-fructosan (i.e. D-fructose - 1 H_2O). If it is heated rapidly to around 200°C, a whole series of decomposition products are formed and caramel is produced.[63,64]

1.9.1.3. Maillard reaction[65]

The reducing sugars formed from sucrose are known to react with amino acids and proteins.[66,67] This is one of the most important types of reactions in food preparation and yields a family of brown-coloured products, known as melanoidins along with various volatile compounds which have strong odours and flavour intensities.

1.9.2. Boiling point elevation[68]

An increase in the presence of sugar in a solution has the effect of raising the boiling point. Boiling point elevation is defined as the difference between the boiling temperature of a sugar solution and that of water at the same absolute pressure. The boiling point elevation (BPE) is pressure and concentration dependent. Table 1.2 gives the value of BPE for a range of concentrations at atmospheric pressure.

g of sucrose per 100g of solution	Boiling point elevation (°C)	g of sucrose per 100g of solution	Boiling point elevation (°C)
33.33	0.74	90.00	19.27
50.00	1.79	90.48	20.01
60.00	2.98	90.91	20.70
66.67	4.25	91.30	21.36
71.43	5.57	91.67	21.99
75.00	6.88	92.00	22.58
77.78	8.18	92.31	23.16
80.00	9.44	92.59	23.70
81.82	10.65	92.86	24.22
83.33	11.81	93.10	24.71
84.62	12.93	93.33	25.18
85.71	13.98	93.55	25.64
86.67	15.93	93.75	26.07
87.50	16.84	93.94	26.49
88.89	17.69	94.12	26.88
89.47	18.51		

Table 1.2: Elevation of the boiling point of sucrose [68]

1.10. Sucrose in food products

Many food systems rely heavily on sucrose as a functional ingredient. It is at the same time a sweetener, bulking agent, texture modifier, preservative, flavour and fermentation substrate. The major food applications are as ingredient in chocolate and confectionery (both of them will be treated more in details in Chapter 4), baking and soft drinks. There are numerous other uses which, though minor in respect of volume turnover are important technologically. Examples include the preserving of dairy food, such as ice-cream, frozen and canned foods and alcoholic beverages.

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CHAPTER II

OTHER SUGARS USED IN CONFECTIONERY

The term sugar is used loosely in the sweet industry to indicate sucrose. Sugar is in fact a generic term which is taken to mean any form of carbohydrate suitable for use as a sweetener.[1] Sucrose is the accepted standard of comparison; any other sweetener must be competitive in price, sweetness and other qualities or capitalize on some weakness of the accepted standard.[2] This chapter presents a selection of the sugars used in confectionery in addition to sucrose.

2.1. Honey

2.1.1. Production[1]

Following the collection and transportation of the nectar (a weak sugar liquor) by the bees to the hive, the water evaporates thereby raising the total solid content from a low 14% to between 75-80%. Sugar conversion occurs through the action of the enzymes that have become entrapped in honey. The combs are removed from the hive and transferred to rotary centrifuges which throw off the honey by a low speed spinning action. After straining, a heating process may be given in which the temperature is raised to 70°C. This is done with the objective of reducing excessive crystallisation on storage.

2.1.2. *Composition*[3]

There is a considerable variation in composition encountered among honeys because they represent different floral types. This latter factor can be compounded by differences from one area or country to another in relation to available nectar sources. Table 2.1 gave the average composition of US honeys. The extreme values found among samples are shown in the column "range". A better idea of variability may be obtained by use of the standard deviation (S) in the table. The composition of Portuguese and Spanish honeys has also been studied by Mendes *et al.*[4] and Mateo *et al.*[5] respectively.

Component	Average	Standard deviation (S)	Range
Moisture	17.2	1.5	13.4 - 22.9
Fructose	38.2	2.1	27.2 - 44.3
Glucose	31.3	3.0	22.0 - 40.7
Sucrose	1.3	0.9	0.2 - 7.6
Maltose	7.3	2.1	2.7 - 16.0
Higher sugars	1.5	1.0	0.1 - 8.5
Free acid	0.43	0.16	0.13 - 0.92
Lactone	0.14	0.07	0.00 - 0.37
Total acid	0.57	0.2	0.17 - 1.17
Ash	0.169	0.15	0.020 - 1.028
Nitrogen	0.041	0.026	0.000 - 0.133

Table 2.1: Average composition of U.S. honeys and range values[3]

The average moisture content is 17.2%. To protect honey from microbiological spoilage this value must not exceed 21% for most floral types.[6] The largest portion of the dry matter in honey consists of sugars. In the main, the sugars are responsible for much of the physical nature of honey, its viscosity, hygroscopicity, granulation properties and energy values.

In nearly all honey types, fructose predominates; a few honeys appear to contain more glucose than fructose. These two sugars together account for 85-95% of honey carbohydrates. The evolution of fructose and glucose in honey over time has been studied. Nevertheless, contradictory results were found. Cavia *et al.*[7] reported an increase in fructose and glucose contents over one year whereas Donner[8] and Jimeney[9] described a decrease of monosaccharides below their original values. More complex sugars made up of two or more molecules of glucose and fructose constitute the remainder. Research has shown that at least eleven disaccharides are present in honey in addition to sucrose.[10] As a natural product, honey has been prone to adulteration, which consists of substituting honey with cheap invert sugars, the most common being cane and beet invert syrups.[11]

2.1.3. Crystallisation

Glucose monohydrate spontaneously crystallises from many honeys, which are supersaturated solutions under ordinary storage conditions. Whether they are also supersaturated under hive conditions at higher temperature is not known, possibly because the carbohydrate composition of honey is more complex than the model systems examined to date[12]. Crystallisation of honey, commonly called granulation, is an undesirable process in liquid honey because it affects the textural properties, making it less appealing to the consumer and in many cases, it results in increased moisture of the liquid phase which can allow naturally occurring yeast cells to multiply which causes the fermentation of honey.[8]

A possible route to understanding honey granulation lies in a study of phase relationships in model systems of sugars. An early attempt was that of Jackson and Silsbee[13], who studied several systems at 30°C, and discussed saturation relationships in honey based on data from the glucose-fructose-water system. They found that glucose solubility decreased with increasing fructose concentration. They concluded that all honey is supersaturated at 23°C. Later Kelly[14] proposed that the presence of fructose had the effect of reducing the transition temperature of glucose monohydrate from above 50°C to something less than 30°C for solutions saturated with fructose.

Extent of granulation	G/W
None	1.58
Few scattered crystals	1.76
1.5 - 3 mm layer of crystals	1.79
6 - 12 mm layer of crystals	1.83
Few lumps of crystals	1.86
1/4 of depth granulated	1.99
3/4 of depth granulated	2.06
Complete soft granulation	2.16
Complete hard granulation	2.24

Table 2.2: Average glucose/water ratios for honeys classified by granulation characteristics[12]

All attempts to predict the granulation behaviour of a particular honey have been empirical, using various proposed indices to fit granulation behaviour observed after storage. Using statistical procedures, White[15] showed highly significant correlations between granulation tendency and several previously proposed indices, the G/W (glucose/water) ratio giving the highest value. The F/G (fructose/glucose) ratio, much used in the past, was the lowest ranking index. When G/W is equal or below 1.58, there is no granulation. Above this value, crystals begin to form and reach complete granulation for G/W = 2.16 (Table 2.2). Differential Scanning Calorimetry (DSC) has been found to be an appropriate tool to determine the rate of crystal growth and the kinetics of honey granulation.[16]

Granulation of honey can be initiated by the introduction of fine seed crystals into liquid honey, acting as nuclei for growth under controlled crystallisation. This process, known as induced granulation, is normally carried out by seeding the liquid honey with 10% of finely crystallised honey, which shows crystallisation compatibility when moisture is less than 18.5% and the ratio G/W higher than 1.8.[17]

2.1.4. Honey in food products[1]

Honey was once widely used for the manufacture of sugar confectionery products but it is now only present in recipes of certain speciality sweet products. Clear honeys which contain no crystal phase have no advantage to the confectioner. The amount of honey that should be incorporated in a sweet should be preferably held under 20%. A 10% addition is sufficient to achieve a satisfactory contribution to the flavour of the product without adversely affecting storage properties. The confections that are produced using honey usually have a softer texture and a more yellow colour.

2.2. Glucose

2.2.1. Production[1]

The main steps for the production of glucose are shown in Figure 2.1. Glucose is produced from starch. In Europe, maize starch is the most common source though potato and wheat starch are also used. Whatever the source of the starch, it comprises two distinct fractions: amylose, in which the anhydroglucopyranose units are linked exclusively in the 1-4 positions, giving a linear molecule, and amylopectin, which is branched due to the presence of 1-6 links. The molecular weight and ratio of these two fractions determine the rheological properties of the starches but have only limited effect on the hydrolysis of starch.

To produce glucose, the starch must be completely hydrolysed. In practice and using acid catalysts, this is never fully achieved, due to side reactions, of which the rates increase markedly during the final stages of hydrolysis when substantial quantities of glucose have been formed.

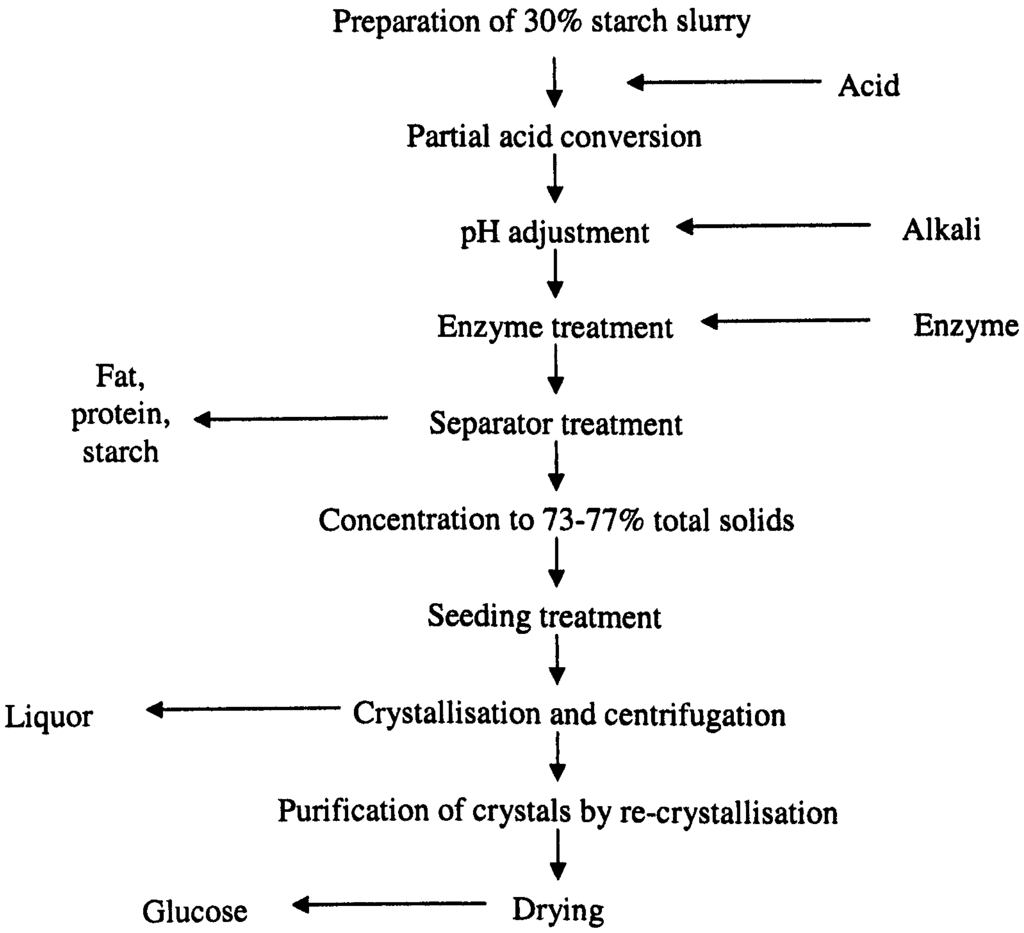

Figure 2.1: Manufacture of glucose[1]

To increase the conversion rate, it is necessary to use lower concentration of starch slurries compared to those used in the manufacture of glucose syrup. With converter pressures of 45 lb/in^2 a maximum DE (Dextrose Equivalent) of 90 is quickly attained. The final stages in processing are concentrating to 76.5% of solid content, cooling and crystallisation.

2.2.2. Mutarotation

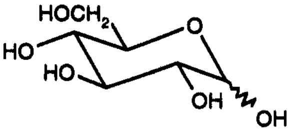

Figure 2.2: α/β-D-glucopyranose molecule

Contrary to sucrose, glucose is a reducing sugar. In an aqueous solution, it undergoes a number of variations which include the transformation between the α and β anomers of the pyranose and the furanose forms, each of which pass by the acyclic form. Glucose shows relatively simple mutarotation behaviour, since the pyranose form of the sugar predominates over the furanose form in solution. For D-glucose at 20°C, the equilibrium composition is 36.2% α and 63.8% β-glucopyranose.[18] Another source give the percentage of β at equilibrium at 66%.[19] If part of the α anomer is crystallised out, another part of the β anomer converts into the α according to the scheme of Figure 2.3. This reaction is of the first order.

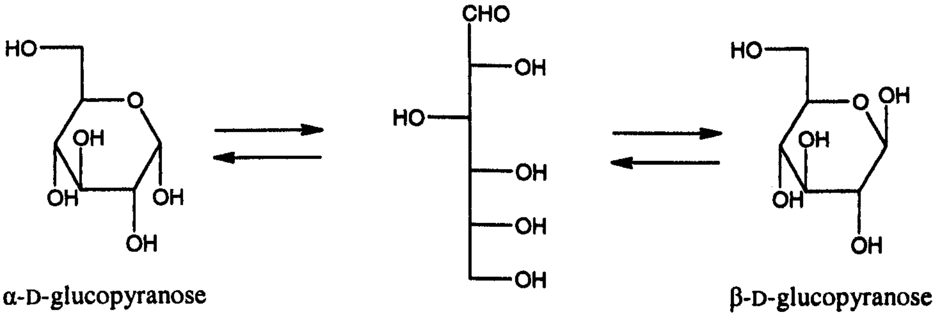

Figure 2.3: Mutarotation of glucose

It has been proposed that much of the anomeric preference of monosaccharides may be determined by solvation effects. A model of pyranose solvation has been proposed, which assumes that axial hydroxyl groups are less favourably hydrated than are equatorial ones.[20]

These equilibrium values depend on the conditions in solution including the temperature, concentration, pH and presence of foreign substances. It has been found that the concentration has no significant effect on the rate constant for mutarotation, whereas increasing temperature enhanced the mutarotation rate of D-glucose solutions.[21]

2.2.3. Solubility and phase diagram of glucose

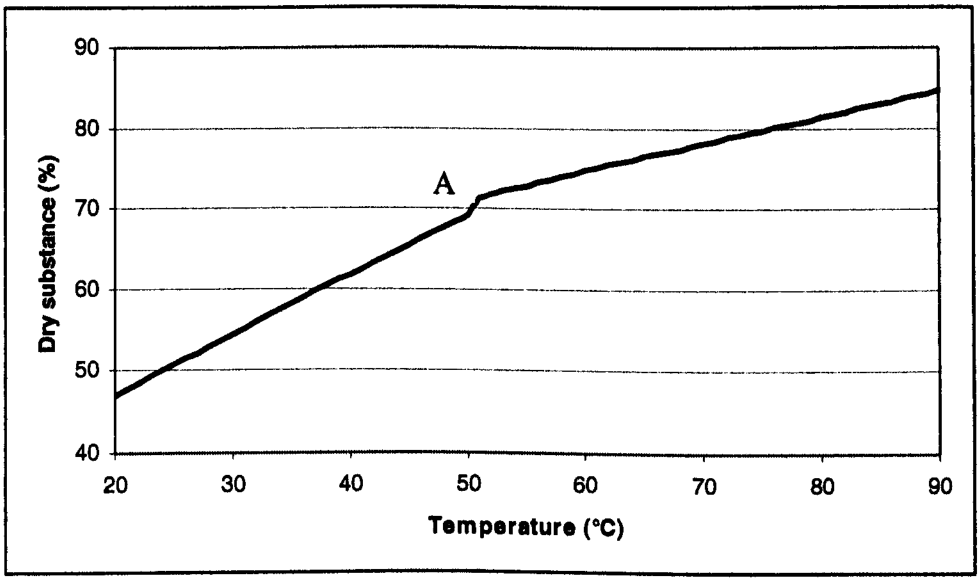

Figure 2.4: Solubility curve of glucose in water[18]

Figure 2.4 shows the solubility curve of glucose. The discontinuity (point A) in the curve of glucose arises due to the occurrence of various forms. Below 50°C α-D-glucose monohydrate is the least soluble component and the solubility curve gives the α-D-glucose monohydrate concentration. Above 50°C however α-glucose anhydrous is the least soluble and the solubility curve reflects the concentration of this different component.[18] The phase diagram of glucose has been studied by Young[22] and is shown in Figure 2.5. Several forms of α-D-glucose crystals exist as well as the β-anhydrous form. An unstable crystalline phase of D-glucose has been found during the study of the system D-glucose-water which is believed to be a hydrated form of β-D-glucose. This phase causes much difficulty in the commercial production of crystalline D-glucose.[23]

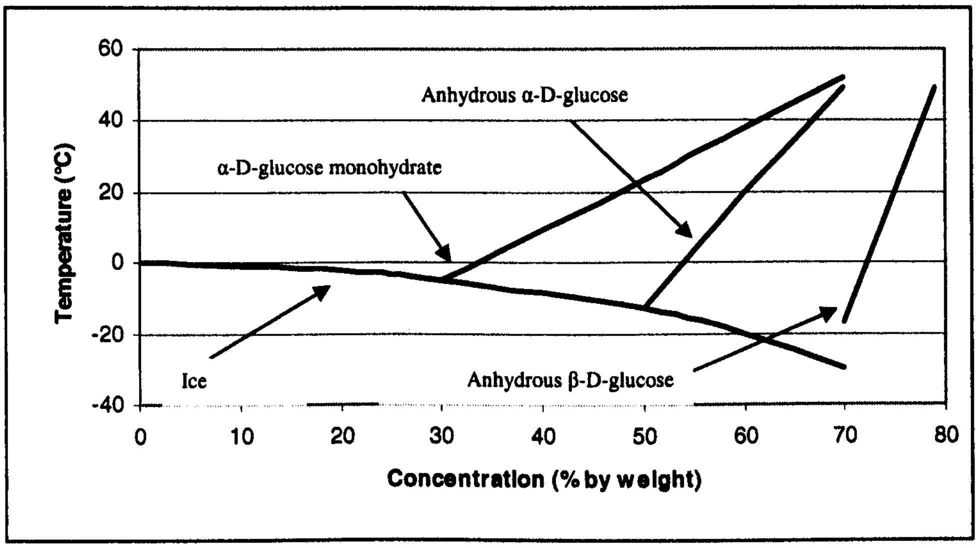

Figure 2.5: Phase diagram D-glucose-water[18]

2.2.4. Metastability

While the metastable region for commercial glucose has been reported to be extremely small by Dean and Gottfried[24], metastable zones for pure glucose solutions that are significantly larger than sucrose have been demonstrated experimentally by Horn[25]. The region of metastability of glucose depends on the equilibrium form of the glucose crystal that is present at a particular temperature and concentration. At lower temperatures and concentrations, a relatively wide metastable region was observed for the glucose hydrate form. At higher temperature and concentrations, the anhydrous glucose had a slightly reduced zone of metastability. However in general, the metastable zone for glucose was similar to that observed for sucrose.

2.2.5. *Crystallisation*

Figures 2.6 and 2.7 show the difference in morphology of a glucose monohydrate crystal and an anhydrous crystal.

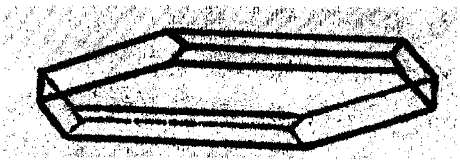

Figure 2.6: Glucose monohydrate crystal[25]

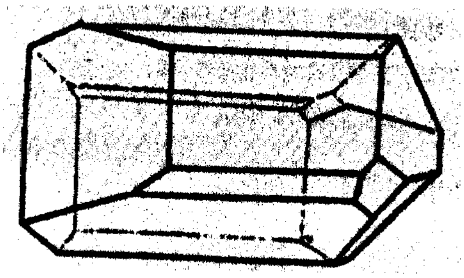

Figure 2.7: Anhydrous glucose crystal[25]

2.2.5.1. Nucleation

The spontaneous nucleation behaviour of glucose monohydrate from solutions has been discussed by Horn[25]. The supersolubility diagram for glucose monohydrate was developed with supersaturation units (SS) given in grams of glucose per 100 g of water. Here, the boundary for metastability is given as somewhere between SS = 1.7 and 2.6 over the temperature range of 0 to 32°C. At supersaturations in this metastable range, nucleation can only occur by a secondary nucleation mechanism, whereas supersaturations of 4.0 are required for spontaneous nucleation. This compares to the value of supersaturation for spontaneous nucleation of sucrose based on SS units of 1.4. Obviously, glucose monohydrate can withstand considerably higher supersaturations before undergoing nucleation.[18] As supersaturation increases; the extent of nucleation initially increases. As supersaturation is further increased, the effect of viscosity (mass transfer) slows down the extent of nucleation until, at extremely high supersaturations, nucleation is totally inhibited. This condition leads to the formation of a glucose glass.

2.2.5.2. Growth[18]

The growth of anhydrous α-glucose crystals is exceedingly slow, compared to sucrose. The rate was seen to increase slowly with increasing temperature. Van Hook[26] showed that growth rate data for α-glucose monohydrate are essentially independent of temperature and increase approximately linearly with increasing supersaturation. From these results he concluded that diffusion of glucose molecules is the rate limiting step for crystal growth under such conditions.

2.2.6. Elevation of the boiling point

Figure 2.8 shows the boiling temperature of glucose solutions compared to sucrose. One can see that to achieve the same concentration as sucrose, the glucose solution needs to be heated at a higher temperature.

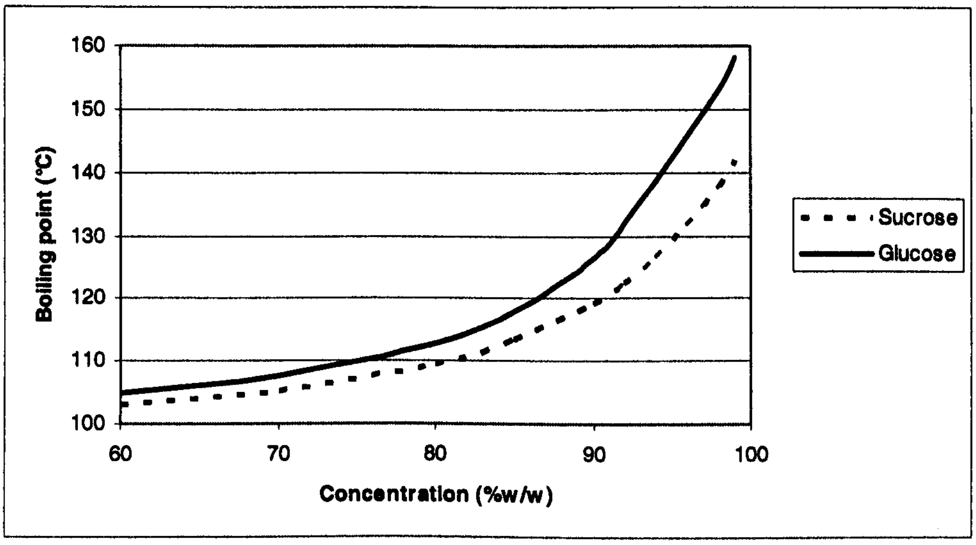

Figure 2.8: Boiling curve of glucose and sucrose[27]

2.2.7. *Glucose in food products*[1]

In confectionery, glucose can be used to promote crystallisation, lower the overall crystal size present in the solid phase and therefore tenderise the sweet. For example, glucose monohydrate is sometimes used as an alternative to sucrose in chewing gum. The endothermic heat of solution of glucose gives a cooling effect in the mouth which is a property that goes well with mint flavours but not with others. The incorporation of glucose will increase the likelihood that crystallisation will occur either on storage or during manufacture.

2.3. Glucose syrups and starch hydrolysates[1]

In the USA glucose syrups are known as corn syrups. Despite the name the major ingredient is not glucose but maltose. Starch hydrolysates are dried conversion products available in a powdered form.

2.3.1. Production of glucose syrups

The origin of glucose syrups is starch. Before the use of enzymes, starch was hydrolysed by the use of mineral acids which is regarded as a more random type of hydrolysis. Furthermore, low DE conversion products of acid hydrolysis contain more glucose than their enzymatically produced counterparts at the same DE.[28] The ability to degrade starch solely by enzyme action came in the mid-1970s with the advent of highly thermostable, bacterial α-amylases. An extended and invaluable range of spray dried products, widely used in the food and confectionery industries thus came available. The use of enzymes with different specificity towards hydrolysing starch is the most important tool in providing a saccharide with a specific composition.[29]

After the conversion of starch by either acid or enzyme catalysed hydrolysis, a detailed process of purification takes place. Initially the conversion takes place at 30-40% concentration, and the sugar solution has to be clarified to remove the protein and lipid fractions which have been liberated from the starch granule during conversion.

These fractions are removed by rotary vacuum filtration or centrifugation. The final stage of refining is the area where the traces of organic impurities are removed. Traditionally this was done by using activated carbon. In more recent developments, however, ion-exchange resins are used to remove almost all the organic and inorganic impurities in glucose syrups.

2.3.2. Classification of different syrups[1]

The conversion of starch is controlled by measuring the proportion of the syrup that gives a Fehling's titration and assuming it to be dextrose (i.e. glucose). Thus these syrups are specified in terms of Dextrose Equivalent, normally abbreviated as DE. Up to

20 DE starch hydrolysates are normally referred to as maltodextrins. Above 20 DE they are more commonly termed spray dried glucose syrup solids. Table 2.3 shows the different types of glucose syrups and their carbohydrate composition.

Type	Low DE	Low DE	Regular DE	Intermediate DE	High DE	High maltose
DE	26	38	42	55	64	42
Monosaccharides	8.0	15.0	19.3	30.8	37.0	5.9
Disaccharides	7.5	12.5	14.3	18.1	31.5	44.4
Trisaccharides	7.5	11.0	11.8	13.2	11.0	12.7
Tetrasaccharides	7	9	10	9.5	5	3.3
Pentasaccharides	6.5	8	8.4	72	40	1.3
Hexasaccharides	5.0	7.0	6.6	5.1	3.0	1.5
Heptasaccharides	4.5	5.0	5.6	4.2	2.0	1.0
Octasaccharides and higher saccharides	54	32.5	24	11.9	6.5	29.4

Table 2.3: Carbohydrate composition of glucose syrups[1]

The properties of glucose syrups and starch hydrolysates depend mainly upon the degree of conversion (DE). Table 2.4 shows the increasing effect upon particular properties of starch hydrolysates. Nevertheless, the dextrose equivalent of a maltodextrin has been shown to be inadequate to predict product performance in various applications.[30]

Property	DE 15 - - - - - - - - 45
Sweetness	⟶
Viscosity	⟵
Moisture pick up	⟶
Crystallisation prevention	⟵
Browning	⟶
Freezing point depression	⟶

Table 2.4: Relation of DE to functional properties of starch hydrolysates[1]

2.3.3. Glucose syrups and starch hydrolysates in confectionery[1]

Glucose syrups have largely replaced invert sugar as a confectionery ingredient. The commonest type of glucose syrup used in sugar confectionery is 42 DE. This material is even referred as confectioner's glucose. 42 DE provides not only bulk but also a source of reducing sugar and improves the product's shelf life by lowering the water activity. Starch hydrolysates have several uses in confectionery. Principally they find application as a filler, carrier and sweetness reducer. They have other functions. Indeed, experience indicates that below 75% of solid contents, certain moulds and yeasts grow in carbohydrate solutions and spoilage will result. The saturation solubility of sucrose in water at 20°C is only 67.1%. Thus sucrose alone cannot give a product with a solid content sufficiently high to prevent microbiological spoilage. To alter this and suppress crystallisation in a solution with a solid content of 75% or over at normal temperatures, a sugar other than sucrose is added. This process is known as "doctoring". The addition of another sugar also prevents the appearance of undesired crystals in some types of confectionery especially high-boiled sweets, which is called graining. Some confections must have some grain for them to have their traditional form, for instance fondants. It is on the production of a very large number of very small sucrose crystals that the smoothness of the fondants depends. To achieve this, the degree of addition of glucose syrup is less important than in high-boiled sweets.

2.4. References

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CHAPTER III

CO-CRYSTALLISATION

3.1. Modification of the sucrose crystal structure

In the early 1960s, researchers began to search for a technology that could add another dimension to the existing sugar crystal. This course of research led to a review of the basic properties of sucrose crystallisation, through which investigations determined that spontaneous crystallisation[1] resulting from rapid agitation of a supersaturated purified sugar solution produces an aggregate of microsized crystals. Initial studies of the aggregate revealed a sponge-like appearance with considerable void space and increased surface area.[2]

One of the first processes reported[1] involved the preparation of a granular, free-flowing, non-caking sugar product comprised of aggregates of fondant-size sucrose crystals. An example given was a free-flowing brown sugar product. Brown sugar is notorious for its problems of sticking and caking. Indeed, brown sugar contains molasses-like components that are hygroscopic. A solution to this problem is to crystallise the sugar to extremely fine crystals. In this way, although the proportion of the molasses-like components would remain the same, the distribution over the increased surface area per unit weight creates a thin film which prevents the problem of caking.

The process involves concentrating a sugar syrup at a temperature in the range 120-130°C to achieve a solid content in the range of 91-97% by weight. The resulting concentrated sugar syrup should contain not more than 15% by weight non-sucrose solids. The concentrated syrup is then subjected to impact beating. Figure 3.1 shows a drawing of the beater crystalliser used in this invention.

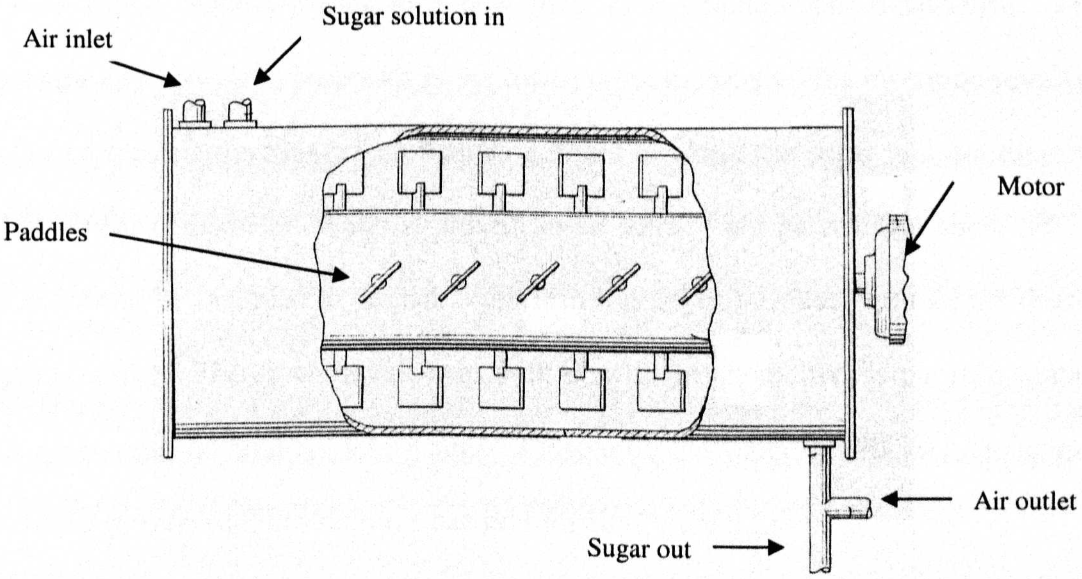

Figure 3.1: Beater-crystalliser[1]

The essence of the operation of the beater-crystalliser is a combination of impact, turbulence and shear to effect very rapid crystallisation of the sugar solution into granules. The unit is run at about 1000 RPM and air is forced through the beater crystalliser to keep the temperature of the material below a critical limit and remove the moisture. The product is then cooled, dried, milled and screened.

Another process[3] for the production of crystalline sugar, which is an improvement over the transformation process, consists of concentrating a sugar syrup until it becomes supersaturated and then crystallising it by mechanical means. Initially, this process was not suitable for a continuous operation. Nevertheless, by subjecting the sugar syrup to a shear force having a velocity gradient of at least 5000 sec^{-1}, instead of below 1000 sec^{-1} as in previous processes, the transformation can be carried out continuously. The shear force has a velocity gradient of preferably at least 20,000 sec^{-1}. The equipment generating the shear force, a colloid mill or a homogenizer, is arranged to operate with the sugar syrup passing through it as fast as possible (0.05-0.5 sec). As a result, the product obtained is a soft, moist, friable solid with an open structure.

A more recent process relates to a new form of crystalline spheroidal sugar.[4] The advantage over previous processes is the lower input in energy. The invention involves the use of ambient systems which include a liquid in which the sugar will not dissolve and a solvent component. Water is present in an amount not greater that about 5%. A surfactant can be included to prepare a uniform tiny crystal product with a high degree of predictability. The amorphous sugar, with or without an additive is put into contact with a non-aqueous liquid in which sugar is insoluble and water. In this way, the unique spheroidal polycrystallite structures can be formed (Figure 3.2).

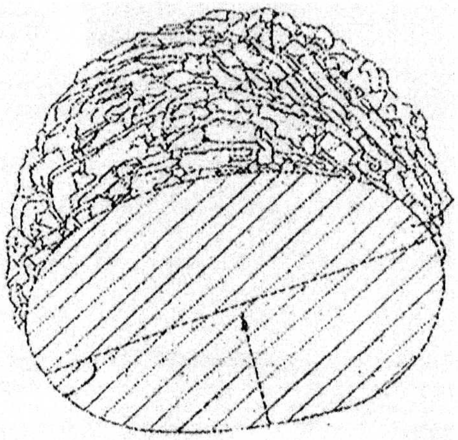

Figure 3.2: Spheroidal sugar[4]

In another process, sugars and sugar alcohols are crystallised in a way that gives unbroken monocrystals with a regular geometry shape and well-defined particle size.[5]

The method is composed of the following steps:

- Production of a concentrated syrup

- Reduction of pressure
- Evaporation under pressure with vigorous agitation in the crystallisation zone
- Stopping evaporation and maintaining agitation
- Resumption of evaporation and agitation until a dry product is obtained.

The product obtained, in addition to consisting of unbroken crystals, has a good rate of dissolution and is non-caking.

Using the process applied to form a free-flowing brown sugar[1], researchers have discovered that crystallisation of sucrose in the presence of a second ingredient created an infinite dispersion of this ingredient over the entire surface area of the new aggregate. This unique phenomenon improved the properties of the second ingredient and was termed co-crystallisation.[6]

3.2. Co-crystallisation involving sucrose: the process

3.2.1. Methodology

While the principle of crystallising a sugar is to purify the crystals, the principle of co-crystallisation is to incorporate a secondary ingredient.

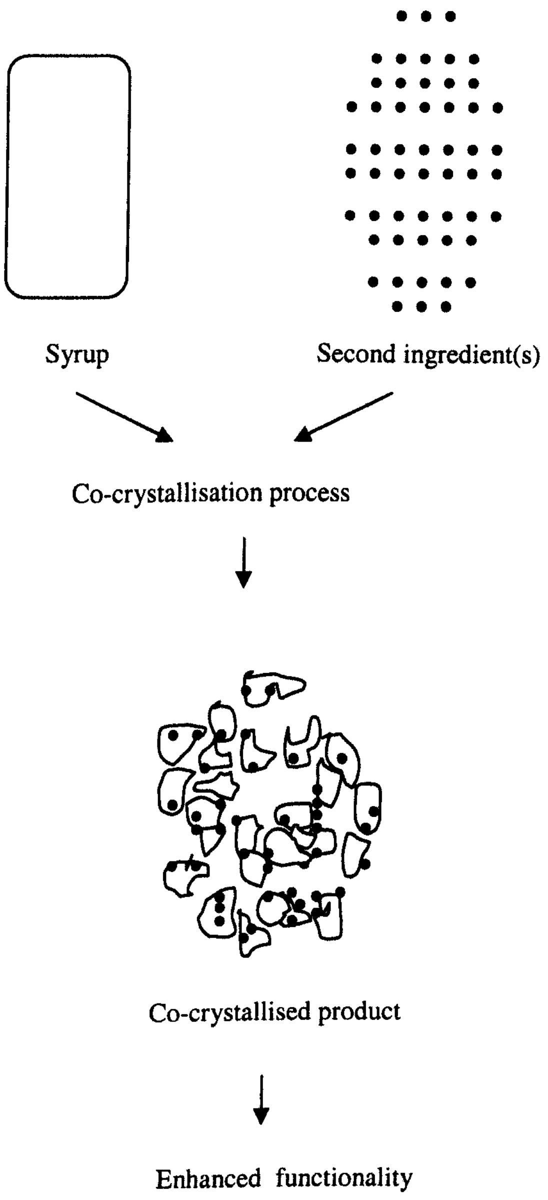

Figure 3.3: Concept of co-crystallisation[7]

The process begins with a sucrose syrup, which is concentrated to a supersaturated solution of 97° Brix (% of sucrose by weight) and heated over 121°C for a few seconds. A second ingredient is then added to the concentrated syrup with vigorous mechanical agitation providing nucleation for the sucrose-ingredient mixture to crystallise subsequently. As cooling proceeds, crystallisation takes place spontaneously without seeding. This process is completed in a few seconds. The sucrose forms tiny crystals that are 3-30 microns in diameter[6,7]. These crystals are then agglomerated in a loose and lacy network and bonded together by point contact. The aggregate formation from microsized crystals allows the inclusion or entrapment of all non-sucrose material within or between them.

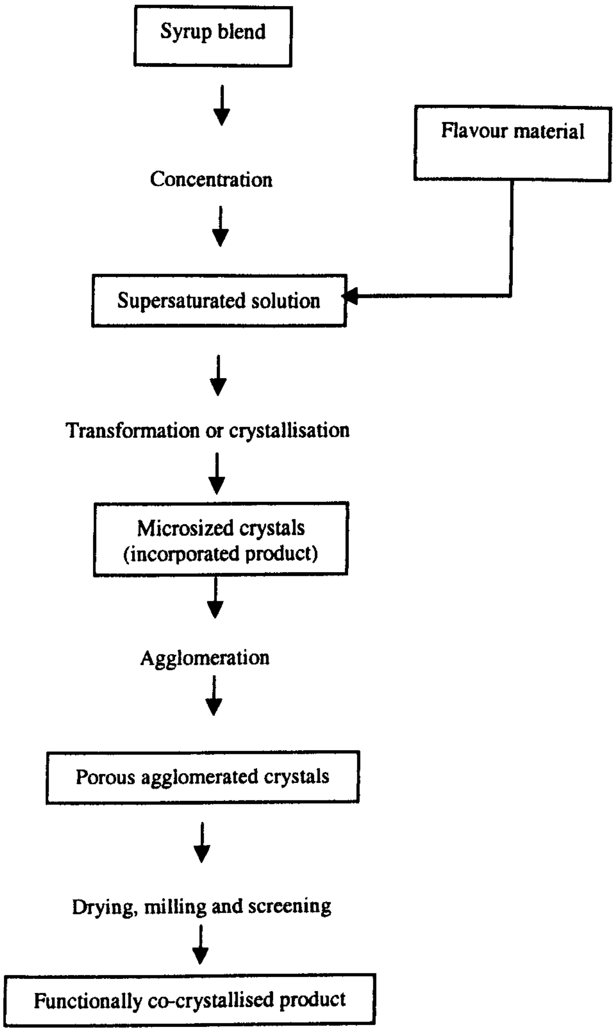

Figure 3.4: Essential steps for the preparation of a co-crystallised flavour[7]

The process requires proper control of the rates of nucleation, crystallisation and thermal balance during the various phases. Careful selection of the second ingredient(s) in the crystallisation process is very important. The ingredient plays two distinct roles in the production of the co-crystallised product: first, it inhibits premature crystallisation, thereby allowing crystallisation to occur at a controlled reproducible rate and second, it greatly enhances the functionality of the co-crystallised product [6].

3.2.2. Second ingredients used

The first patent reported the preparation of a tabletting sugar[8] made up of fondant size sucrose crystals in the range of 3-50 microns and containing 0.5 to 7.5% of maltodextrins. The recovered crystals had less than about 2.5 to 3% of moisture and were dried to about 1%.

A similar method is disclosed where a premix consisting of an active ingredient (e.g. a volatile flavour, an enzyme, an acidic substance such as ascorbic acid, a fruit juice concentrate, or a high invert sugar substance) is mixed with a concentrated sugar syrup. The combination is subjected to impact beating until a crystallised sugar product made up of fondant-size sucrose crystals and the active ingredient is formed.[9]

Furthermore, the same process is used for preparing a crystallised sugar product containing a food ingredient.[10] The food ingredient, such as gelatine, cocoa powder, pectin concentrate, etc, is admixed with the sugar syrup, the mixture is subjected to impact beating until crystallised sugar products, made up of aggregates of fondant size sucrose crystals and food ingredient, are formed.

In addition, US Patents 4,159,210[11] and 4,423,085[12] disclosed co-crystallised products composed of maple sugar and sugar nut respectively.

N-(*N*-(3,3-Dimethylbutyl)-L-α-aspartyl)-L-phenylalanine-1-methylester was also co-crystallised with sucrose.[13] The process involves the preparation of a supersaturated solution of sugar to which a premix of neotame and sugar is added prior to crystallisation. Nucleation is induced by vigorous mechanical agitation applied with either a Hobart mixer or a turbilizer. The agitation is carried on with quick cooling. In the product obtained, the neotame is said to be incorporated as an integral part of the sugar matrix and there is no tendency for the neotame to separate or settle out during storage or handling.

3.2.3. Structure of a co-crystalline product[6]

The co-crystallised product consists of aggregates of microsized crystallised lattice structures. These agglomerates have loose porous clusters of very small individual syrup coated sugar crystals bonded together at their interfaces by point contact. A multiplicity of voids and interstices extends between the agglomerates throughout the structure. In the structure, the sugar crystal formation separates the particles of the additive ingredient from one another, thereby preventing the particles, which have normally a great affinity for water, from agglomerating. Consequently, an aqueous solution can rapidly penetrate the agglomerates.

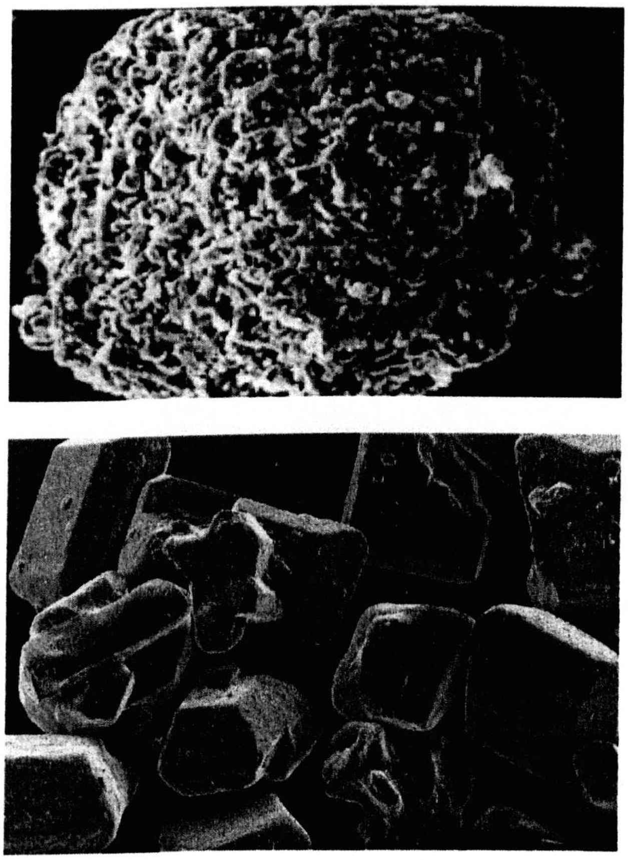

Figure 3.5: Photomicrographs of a co-crystallised product at 175× magnification[6] (top) and granulated sucrose at 33× magnification (bottom)

3.2.4. Properties of a co-crystalline product

In general, the co-crystallisation process improves the properties of the ingredients of the material obtained.[14]

Compressible sugar (Di-pac®), a typical co-crystallised product containing 97% of sucrose and 3% of maltodextrins is said to have characteristics distinctly different from those of the direct compaction sugars.[2] Due to its porous structure it is affected by small changes in moisture content. The moisture level affects the compressibility of the product. Table 3.1 shows the compression force, unit ejection force and hardness of tablets prepared with Di-pac® at different moisture contents. The high moisture levels provide greater compressibility and lower ejection forces.

Moisture content (%)	Compression force (kg)	Unit ejection force (kg/cm^2)	Hardness (kg)
0.48	295	2.1	6
	590	6.0	10.8
	885	9.6	15.6
	1180	13.7	18.5
	1475	19.4	20.4
0.31	295	4.4	2.4
	590	9.2	3.9
	885	14.3	6.2
	1180	19.2	8.7
	1475	26.1	10.9

Table 3.1: Compression results for Di-pac® at different moisture contents [2]

In addition, the co-crystallisation process helps to overcome the troublesome solubility characteristics associated with food ingredients such as fumaric acid, proteins and starch when dissolved in solution.[6,15] Co-crystallised fumaric acid containing 20% of acid and 80% of sucrose dissolved almost completely in 20 sec in cold water at 20°C (Table 3.2). However, in a physical blend, only 56.5% dissolved over a sixty second period.

Extraction time	Dissolving rate (%)	
	Co-crystalline material	Physical blend
10	96.4	34.5
20	98.2	43.5
30	98.2	49.0
60	100	56.3

Table 3.2: Dissolving rate of a co-crystalline material containing 20% of fumaric acid and 80% of sucrose and a dry blend of the same composition[6]

In another experiment, gas chromatography was used to measure the retention of different flavours in co-crystalline products.[7] Results indicated that there was no significant change in flavour retention for up to 15 weeks of storage.

Another advantage of co-crystallisation is that it can help control the sweetness release of a product. Coating sugar crystals with an odourless, tasteless, high melting point hydrogenated vegetable oil by co-crystallisation produces a product that slowly releases sweetness. Under comparable conditions, regular granular sugar completely releases its sweetness in less than 15 sec, whereas, co-crystallised 90% sugar and 10% oil product takes more than 40 min to achieve the same level of sweetness.[6,14]

Although a number of patents have been reported on co-crystallisation, very few research works have been published relating to the physical properties which characterise and describe the structures of such materials. Beristain *et al.*[16] encapsulated orange peel oil using a co-crystallisation process and conducted a storage test on the resultant product. Although the product had free-flowing properties, the addition of a strong anti-oxidant was necessary to retard the development of oxidised flavours during storage. This result was probably induced by the presence of a large amount of surface oil produced in an attempt to incorporate very high amounts of flavour compounds during co-crystallisation. Chen[7] reported a very low increase in peroxide value of co-crystallised peanut butter compared with a dry blended product with the same amount of peanut butter when both of them were stored for 38 weeks at 39°C.

Beristain *et al.*[17] also studied the co-crystallisation of an extract of the Jamaica flower with sucrose. It was reported that the hygroscopicity of the agglomerates increased as the pH was reduced from 4.3 to 3 and all the flavour and colour were retained in the co-crystallised product.

In another work, honey was co-crystallised with sucrose.[18] The proportions 90:10 and 85:15 produced granular co-crystals whereas the ratio 80:20 produced semi solid products. The granules were found to be relatively free-flowing. Gas chromatography was used to compare the differences in relative amounts of four flavour compounds. The results indicated some minor differences in the quantity of flavour volatiles in honey relative to the co-crystallised product. Therefore, exposing honey to high temperatures during the co-crystallisation process did not induce any severe changes in its flavour composition. Microscopic analysis showed that the co-crystalline materials consisted of droplets of syrup mixed together with co-crystallised agglomerates. However, this report did not cover the crystallisation of the individual honey sugars during the co-crystallisation process: this topic will be discussed in Chapter 5.

In a more recent article, Bhandhari *et al.*[19] co-crystallised sucrose with fructose, glucose and mixtures of fructose and glucose. The study showed that the crystallisation of sucrose was delayed in presence of these lower molecular weight sugars. Samples containing 10, 15 and 20% of glucose in the co-crystallised products demonstrated crystallisation of glucose in its monohydrate form after 1month of storage.

3.3. Attempts to define a co-crystalline phase[20]

In the first instance, it is important to review briefly binary systems. Such systems can be divided according to their phase diagrams into eutectic systems, monotectic systems, systems forming solid solutions and systems forming complexes: i.e., co-crystals.

Phase diagrams are usually determined from heating curve data. Figure 3.6 displays a phase diagram which is typical of a simple eutectic mixture of two hypothetical compounds derived from Figure 3.7 which shows theoretical curves produced by either Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC). Only three compositions display a single melting endotherm and these are the pure components A and B and the composition which represents the eutectic composition.

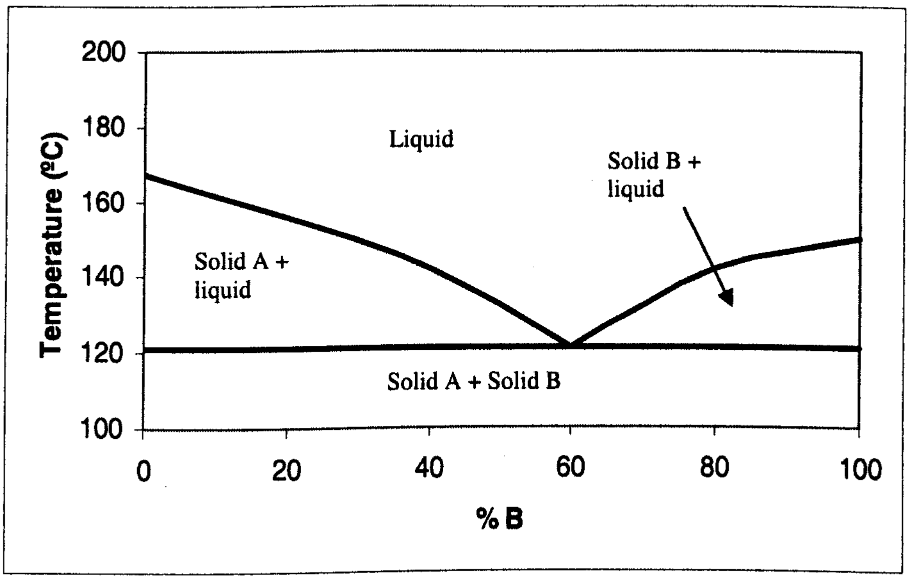

Figure 3.6: Phase diagram of two components A and B showing simple eutectic formation[20]

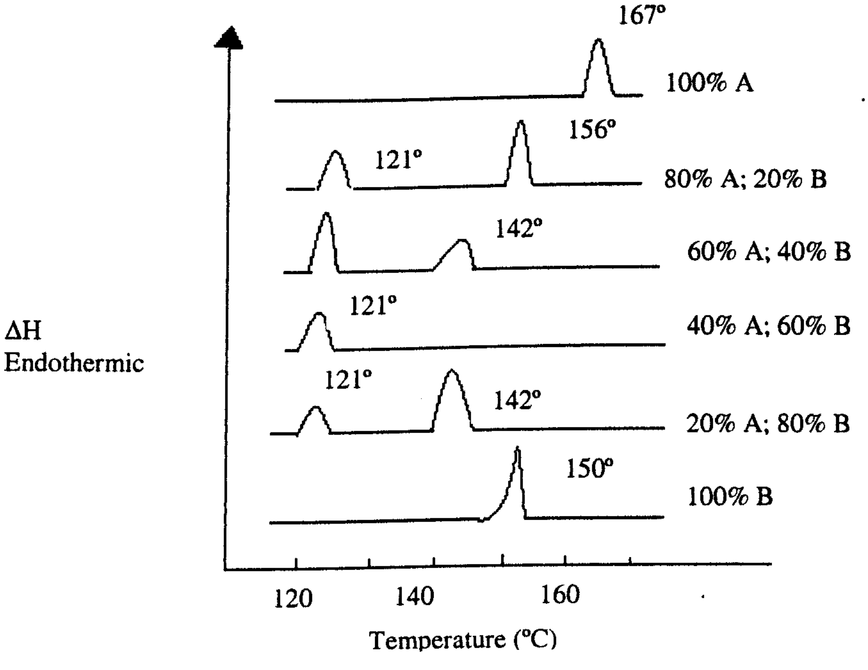

Figure 3.7: DSC or DTA scans used to construct Figure 3.6[20]

For monotectic systems, the phase diagrams are similar to those of eutectic mixtures but with one liquidus arms absent and the other approaching the solidus horizontal at zero concentration of one of the components (Figure 3.8).

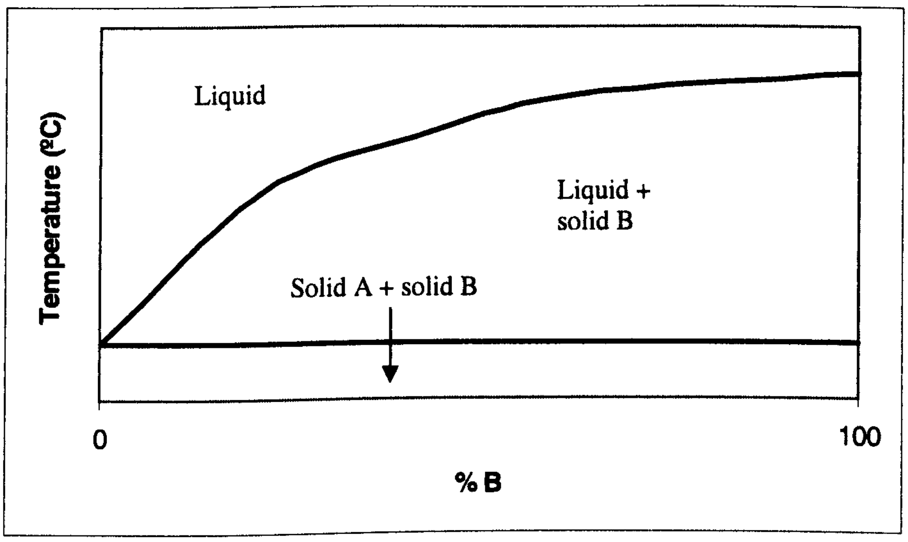

Figure 3.8: Phase diagram of two components showing monotectic formation[20]

Solid solutions represent systems in which there is mutual solubility in both the liquid and solid states (Figure 3.9). They may be either substitutional, when the molecules of one of the compounds replace the molecules of the other in the crystal lattice or held interstitially, where the molecules of one of the compound sit within the crystal lattice of the other without disrupting it.

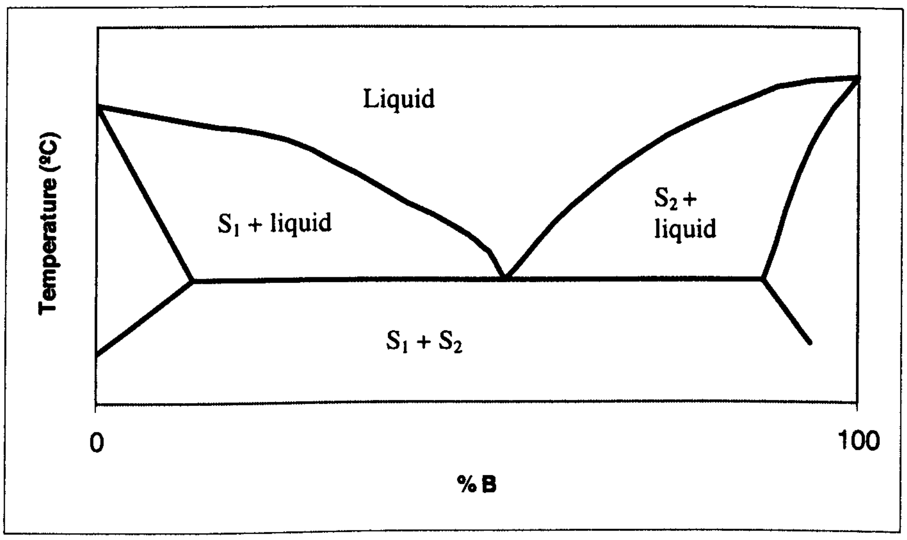

Figure 3.9: Phase diagram of two components showing partially miscible solid solutions with eutectic formation[20]

When two molecules interact significantly with each other, they may form separate stable complexes. In the phase diagram, the existence of a compound with its own melting point is easily distinguished (Figure 3.10). This melting point may be said to be congruous, giving a congruent melting point at the exact stoechiometric ratio of the complex.

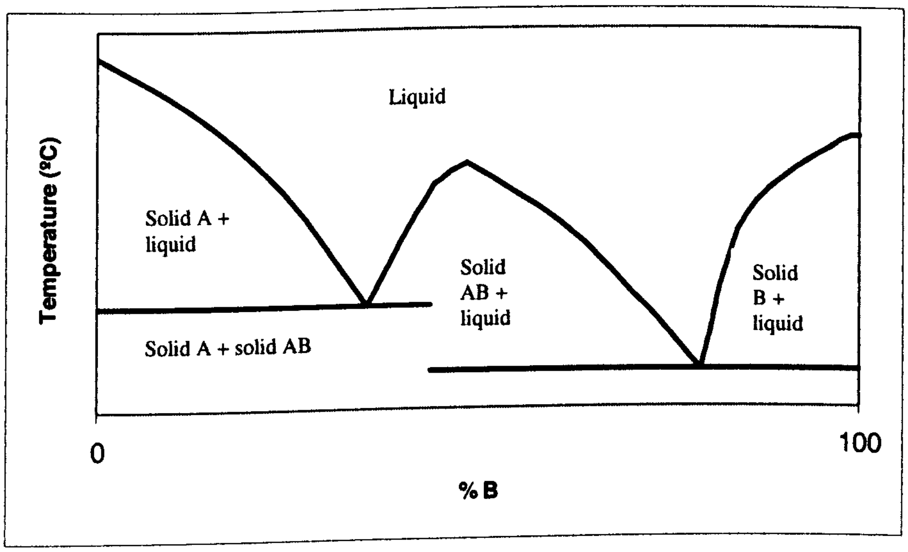

Figure 3.10: Phase diagram displaying complex formation with a congruent melting point[20]

There are many variations in the methods used to analyse phase interactions. Hydrogen bonded co-crystals can be prepared by the blending of two ingredients by gentle triturating. More intimately blended systems may be prepared either by prior fusion and solidification or by dissolving the ingredients in a solvent in which they are mutually miscible. There is no general rule as to which method is the most acceptable.

Differential Scanning Calorimetry experiments performed to investigate the melting behaviour of blends of low density polyethylene (LDPE) and high density polyethylene (HDPE) revealed an additional endothermic peak suggesting the formation of a co-crystalline phase.[21]

Co-crystalline alditols have also been reported to be formed between xylitol and sorbitol.[22] The process consisted of forming a homogeneous molten blend of xylitol and sorbitol, cooling the mixture under agitation until a viscous mass was formed and cooling the mass slowly until sorbitol-xylitol blends became fully co-crystallised. The co-crystallised material obtained by co-melting exhibited melting points several degrees lower than sorbitol or xylitol.

A similar co-melting process was used to prepare a co-crystallised polyol and hydrogenated maltodextrin composition.[23] The composition was said to have improved flow properties and reduced hygroscopicity.

In addition, a co-crystalline sugar formed of sorbitol and mannitol has also been reported. It was done by co-crystallising mannitol with sorbitol melt in a twin screw mixer.[24] Furthermore, mixtures of xylitol, D-sorbitol and D-mannitol have been investigated[25] by grinding the solids together. The phase diagram for the mixture of xylitol-D-mannitol and D-sorbitol-D-mannitol were monotectic. The xylitol-D-sorbitol phase diagram showed that co-crystallisation between these two components could be achieved by grinding them together. It showed the formation of a eutectic phase diagram. The X-ray powder diffraction measurements confirmed that these samples contained, in addition to the pure starting materials, some new product whose appearance could be observed by an extra peak arising in the X-ray powder diffraction pattern.

Moreover, glucose and sucrose have been reported to be co-crystallised onto the surface of breakfast cereal products. In this invention, it was said that glucose and sucrose co-crystallised and did not form mixed crystals. Nevertheless, no physical data was put forward to confirm this statement.[26,27]

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CHAPTER IV

SUGAR CONFECTIONERY AND CHOCOLATE MANUFACTURE

4.1. Tabletting

Tabletting is the area where sugar confectionery and pharmaceutical manufacture come closest; as the machines are similar the processes can also be similar. Confectioners normally try to make tablets as hard as possible whereas pharmaceutical tablets are normally made to be relatively soft.[1]

Tablets are made by compressing powder in a die. The particles bond together under pressure and the compacted tablet is ejected from the die.[2] Figure 4.1 shows the operation of a simple tablet press.

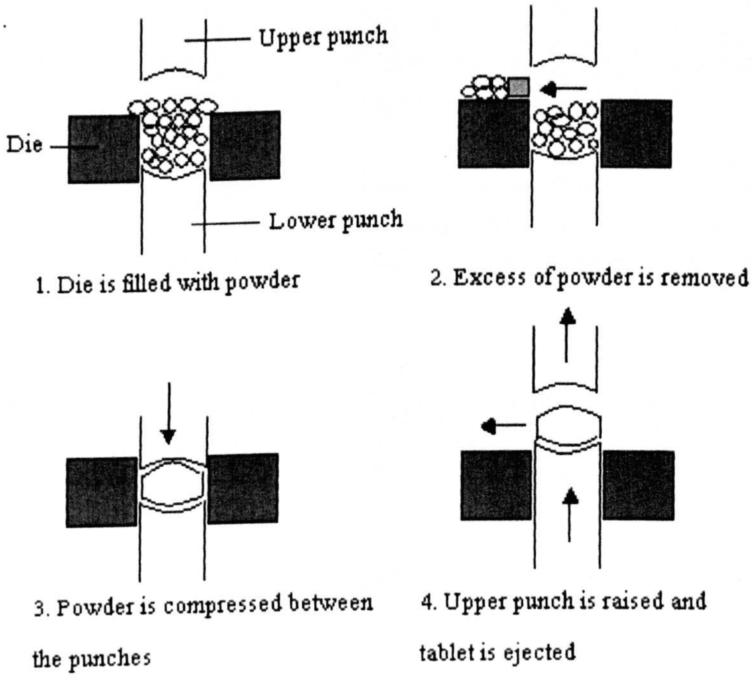

Figure 4.1: Operation of a single tablet press [3]

The die is filled volumetrically, excess material is removed and the powder is compressed between two punches. The lower punch ejects the tablet. To form a tablet successfully, the powder must be free-flowing and yet be capable of bonding strongly under pressure. The bonds between particles must be sufficiently strong to withstand the considerable force required to eject the tablet from the die, and the resultant compact must be hard enough to withstand handling and yet retain favourable "mouthfeel".[4] Certain powders already possess these characteristics and are termed "directly compressible" materials. Other powders may be formed into tablets, but must first undergo a granulation stage.[1,2]

4.1.1. Granulation

The aim of the granulation process is to produce a free-flowing material, suitable for compression. There are several ways of achieving this. The effect of different types of granulation has been studied in relation to: loose density; angle of repose; granule size distribution of powders; tensile strength of tablets.[5] In the case of melt granulation, it has been shown that the granulation variables (process variables: impeller speed; mixing time; mixer load and formulation variables: amount and type of binder; different additives) are the most important for the quality of the tablets rather than the setting of the tabletting machine.[6]

4.1.1.1. Wet granulation

Wet granulation is suitable for most materials, but it is expensive in terms of manufacturing space, time and energy consumption. The powder to be granulated is screened to a uniform particle size and mixed with a granulating solution until a firm dough is formed.

The granulating solution is a binder dissolved in water, which will glue particles together to form granules. Binders are materials such as gum arabic, gelatine, starches and alginates. It is important that mixing is thorough and that the correct amount of binder is added. Too much will cause the granules to be too hard, whilst too little will be insufficient to hold the powder particles together. The correct level of addition is such that the material may be compressed in the hand to form a ball which will not crumble or stick when broken apart. The potential of cold extrusion as a continuous wet granulation technique has been reported.[7-9]

When the mixing is complete the dough is roughly milled to aid the drying process. The granules are dried on trays for up to 24 h at 50-60°C. There are several other methods of drying, including the use of rotary driers, microwaves and fluidised beds, the last being a particularly effective method, as a batch of granules may be dried in just 20-30 min.[2] The drying process needs to be optimised from one product to another otherwise granules can be too porous, bulky and in some cases too fragile.[10]

4.1.1.2. Fluidised bed granulation

A quicker way of granulating is to use a fluid bed granulator for the entire process. With this method, the bed of powder is fluidised in an air stream and sprayed with binder solution. The powder agglomerates into granules, which are subsequently dried in the air stream (the drying air being at 40-80°C). Once the granules are dry, lubricant and flavour may be added and mixed by a further period of fluidisation.[2]

4.1.2. Ingredients

4.1.2.1. Base materials[2]

Numerous materials are available for tablet manufacture; some are available in a directly compressible form, whereas some require granulation. If a particular material does not possess all the necessary properties for tablet formation, several materials may be blended together. Sucrose is available in directly compressible forms, which are expensive, but save on granulation costs. Fructose and glucose monohydrate may be compressed directly. Fructose tablets are soft and break easily. Glucose monohydrate has needle-shaped crystals that form a tightly bound structure when held under compression.[11] Sorbitol and mannitol are also available in directly compressible forms. The tablets have a cooling effect when dissolved in the mouth.

4.1.2.2. Binders[2]

The binder is incorporated in the formulation to enhance the tablet strength and the tablets compressed from granules are known to have higher tensile strength than those compressed from powders.[12] Typical binders are gums such as, gelatine and alginates, but can also be starches, sugars or fats. When using binders, it is important to use the correct amount of solution and to ensure a good mix with the base materials. The effect that the binder will have upon the final tablet must be also taken into account. Certain materials such as gelatine can cause hardening during storage. Binders are not necessary when a material is directly compressible.

4.1.2.3. Lubricants[1,2]

Lubricants are added in order to overcome one of three possible problems. A "glidant" is added to a poor-flowing material to reduce interparticular friction and so improve flow characteristics; it may be added to directly compressible materials or granules. Suitable materials have a small particle size and consequently, a large surface area which allows the glidant to form a coating around the particles of the base material. Silica type materials are glidants. The level of addition is critical, as above a certain level glidants have a detrimental effect upon the flow properties. Furthermore, a study of the effect of anticaking agents on the flow properties of sucrose showed that the cohesiveness of the powder was reduced but its compressibility was reduced too.[13]

Lubricants are added to coat the surface of the tablet and reduce the friction between the tablet and the die wall, thus increasing the ease of tablet ejection. Too much lubricant will reduce the bonding ability of the tablet, whereas too little can cause the tablet to bind in the die.

Lubricants may be added to the base material before compression, or prior to granulation. The latter method usually leads to better dispersion. Lubricants can be materials such as oils or fats, or more frequently magnesium stearate or stearic acid.

The third lubricant action is that of anti-adherents, which reduce the likelihood of the tablet sticking to the punch faces and thus reduce the problem of "picking", where part of the tablet is removed as the top punch is lifted. This problem is most likely to occur when using an intricately embossed or engraved punch face.

4.1.2.4. Flavours

Tablets have a long shelf life and consequently it is essential that the flavouring is also stable for an equivalent period of time.[14] Four types of flavouring are available to the manufacturers of sugar confections: essential oils, essences, fruit juices and pulps and powdered flavours.[15] Essentials oils are mixtures of volatile compounds isolated from plants and animal materials. More than 50% of the quantity of all the essential oils are citrus and mint oil.[16] Essences are either diluted solutions of essential oils or mixtures of the synthetic chemicals blended to match the natural flavour.[15]

For tablet making, liquid flavours can be added to powders and mixed in at the granulation stage, but considerable flavour loss occurs during drying. The liquid may be added to the dry granules or the directly compressible material, but as the flavour is spread over the surface of the granules the increased surface area exposed to the air makes the flavour susceptible to oxidation. A preferable method is to use powdered flavours, where the coating around the flavouring materials provides a protective covering. Flavours most suitable for confectionery tablets are peppermint or fruit flavours.[2]

4.1.3. Compression

The compression process involves applying just sufficient pressure to a material to enable it to bind together and thereby form a firm compact. Tablet presses range from single-punch presses to high speed rotary machines with up to 75 sets of dies and punches. Once the die is filled with material, the pressure is gradually applied. The first stage of compression is when the particles rearrange to fill the voids in the die and trapped air is removed. Once the particles are no longer free to move about, further pressure causes fracture and elastic deformation. During the dwell time of the maximum applied pressure, the clean surfaces of the particles formed during fracture bond together. As the upper punch is removed, a stage of stress relaxation occurs, in which the internal stresses built up in the tablets relax. If these stresses are too great, the tablet will break up on ejection from the die. It has been shown that tablets continue to relax and thus change dimensions up to 100 days after manufacture.

Figure 4.2 shows a typical example of flow sheet of tablet making. Stearic acid and starch are added as lubricant and binder respectively. The powder is prepared by wet granulation followed by drying. The flavour used is mint, added in the form of an oil just before pressing.

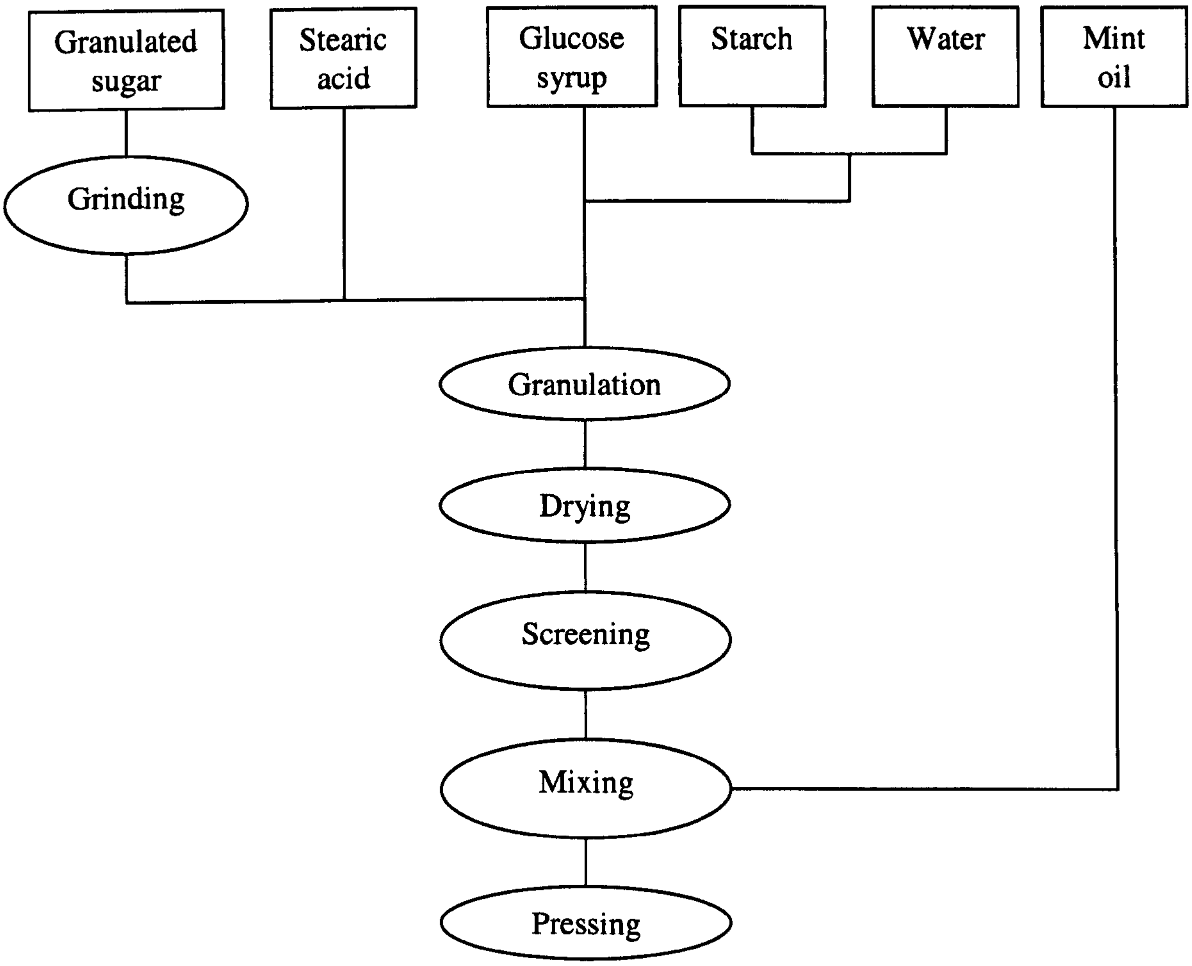

Figure 4.2: Flow sheet of Polo manufacture

4.1.4. Faults[2]

4.1.4.1. Capping

Capping is a frequent occurrence in tablets. The weakest part of the compact is just below the top surface. When the tablet is ejected from the die, as the top portion emerges it may expand, causing a thin layer to separate from the top of the tablet in the form of a "cap". This can be caused by excessive compaction pressure, trapped air, weak bonding between particles as a result of weak granules (i.e. insufficient binder), excessive elastic recovery of the material, or poor machine settings. Lamination is an extreme form of the capping problem whereby the whole tablet separates into many layers.

4.1.4.2. Sticking and picking

Tablets may stick in the die during ejection. This can be overcome by the use of a lubricant or by adjustment of the moisture content of the granules. Small portions of the tablet may be picked off by the punches. This can be due to damaged punch faces or absence of anti-adherent material.

4.1.4.3. Pitting

A certain amount of fine particles is necessary to fill in spaces in the tablet structure; lack of fines can result in the tablet having a pitted surface.

4.1.4.4. Size and weight variation

Variation in the bulk density of raw materials can affect the die fill and the dimensions and weight of the resultant tablet. It is essential that the bulk density is carefully controlled. Secondly, if the material is not flowing evenly, the die fill will also vary.

4.1.5. Flavour retention

The manner in which the flavour molecules are retained during processing and storage are governed by the partition of flavour molecules between phases, the transport mechanisms that carry flavour molecules through food matrices and the binding of flavour molecules to food components.[17]

Flavour interactions have conventionally been considered as occurring within the liquid and air phases. When water is limited, the partition of volatiles between the liquid, solid and air phases is not easy to predict. Low moisture foods tend to have long shelf-lives and the loss of volatiles during storage causes flavour fade, the flavour intensity seeming to decrease with time. This is the case of pressed sweets. The effects of water content and of the type of matrices on the retention of flavours have been studied. Menting *et al.*[18] measured diffusion of volatiles into maltodextrins at a range of moisture contents. They concluded that the diffusion coefficient was dependent both on water content and on the size of the molecules diffusing. Le Thanh *et al.*[19] found that the amount of volatiles sorbed depended on the nature of both the volatiles and the matrix. More recently, the influence of the solid state of the matrix has also been studied. The basis of the theory was that molecular motion is minimal in a glass, so volatile loss might be expected to be minimized during storage if the product was in a glassy state.

Gunning *et al.*[20] showed that essentially all the flavour components behaved in this way in carbohydrate matrices.

4.2. Chocolate manufacture

4.2.1. Ingredients

4.2.1.1. Cocoa nibs, cocoa liquor

Cocoa beans consist of an outer shell surrounding two nibs and a small germ. Cocoa butter accounts for over half of the dry weight of the bean. The moisture content of the bean is about 65%. During the fermentation process the bean is killed so that it cannot be spoiled by germination. In addition certain chemicals are formed. These are known as flavour precursors. Following fermentation the beans must be dried to avoid mould growing on the beans.[21] The main steps of the preparation of cocoa nibs and cocoa liquor are shown in Figure 4.3.[22]

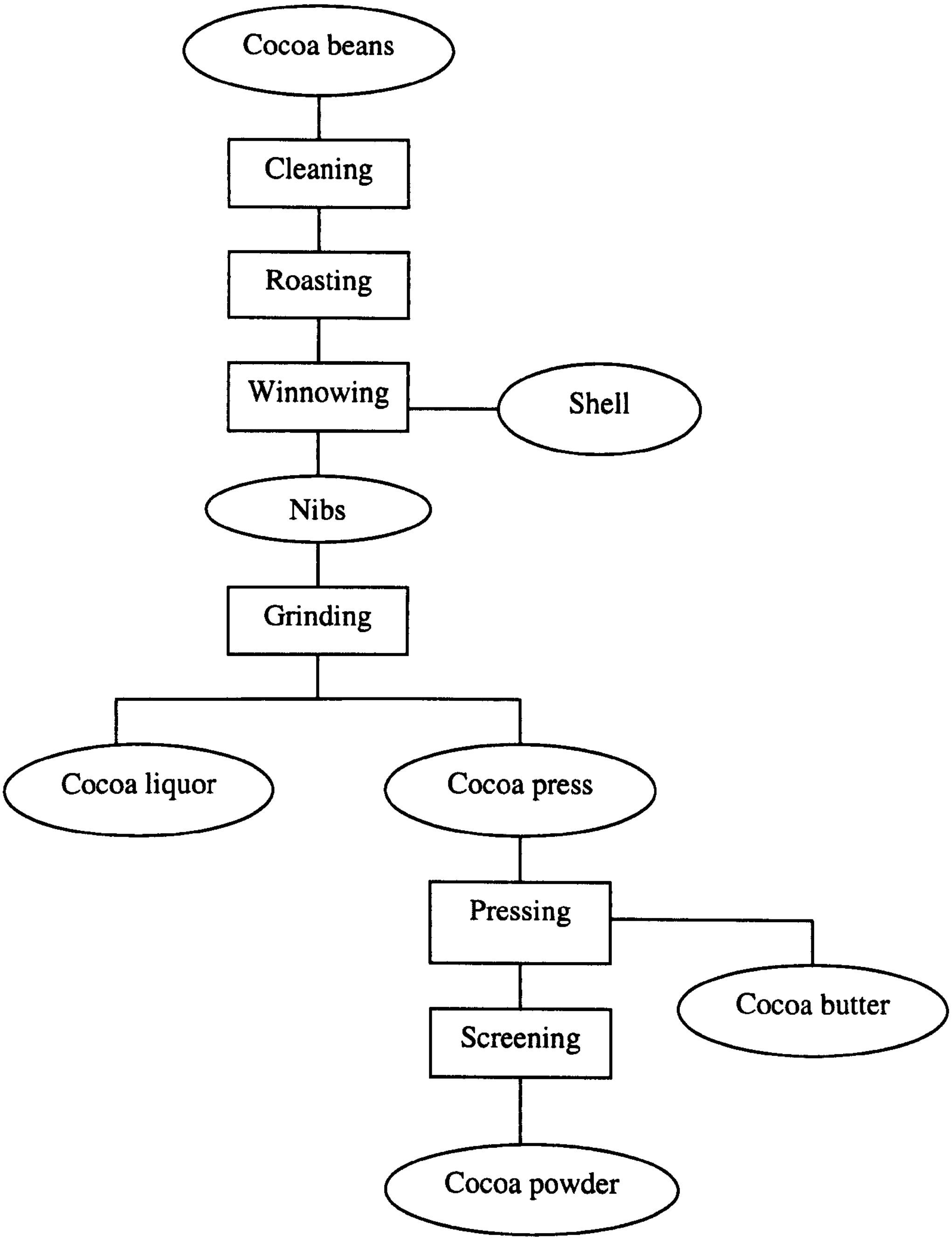

Figure 4.3: Treatment of cocoa beans[22]

4.2.1.1.1. Cleaning[21,22]

It is necessary to clean cocoa beans after delivery to remove any earth and foreign matter that may be present. The process is one of screening, brushing and conveying over powerful magnets. Magnetic separator will take out some of the metallic fragments and metal detector heads will isolate any remaining metallic fragments.

4.2.1.1.2. Roasting[22]

Five changes occur during the roasting of cocoa beans. These are:

- The development of flavouring components which enhance both cocoa taste and aroma
- Textural changes in the shell permitting its removal in subsequent processing
- Development of colour
- Removal of moisture
- Chemical changes in bean constituents.

Roasting was originally carried out by soaking the cocoa beans in water to break the husk. The breakthrough in roaster design came with the large batch open flame heating methods now developed into continuous procedure use, electrical, hot air, and infra-red heating.

Suitable roasting temperatures are 115-140°C. Roasting should be arranged such that the beans are brought up to temperature quickly, held at this temperature for the full period roast and rapidly cooled after discharge. Roasting, as a single process, is insufficient to develop a full chocolate flavour. Beans, which have not been fermented will not develop a chocolate flavour on roasting.

4.2.1.1.3. Winnowing[22]

The purpose of winnowing is to separate the shell and germ and to split the cocoa bean into its natural segments (cocoa nibs). Cocoa beans are first cracked by passing through rollers or rotating cones. An air current is then used to blow away the lighter shell.

4.2.1.2. Sugar

Plain chocolate contains about 50% sucrose suspended in the dry finely divided state in cocoa butter. Sucrose is a cheap filler or bulking agent, providing texture and mouthfeel. The sweetness is used to counter the natural bitterness of the cocoa. In milk chocolate, the role of filler is shared with milk which enables the sucrose concentration to be reduced.[23] High grade sugar should be used in manufacturing chocolate. It must be dry and free from invert sugar.[24] Most manufacturers use a medium fine grain size. There is a strong interest in reducing the amount of calories contained in chocolate or its sweetness.[25] This can be done by reducing the amount of sucrose. Some recipes incorporate fructose for diabetics.[21] Anhydrous glucose is much too expensive for application in chocolate. In addition, it was found that glucose monohydrate could not be used in the chocolate production process due to the vapour development at high conching temperatures. A patent[26] report the addition of glucose monohydrate after the conching step. Spray dried glucose has been used as partial or complete replacement of sucrose in chocolate.[25] It was demonstrated that there was a decrease in viscosity of the final product. Usually, glucose and glucose syrup cause trouble with moisture absorption during refining since they are very hygroscopic. The take up of moisture makes the liquid, melted chocolate very thick, because it tends to stick the sugar particles together.[21,22]

4.2.1.3. Cocoa butter[21]

Most confectionery today is manufactured from vegetable fats. It is traditional to refer to fats that are liquid at room temperature as oils.[27] The main constituents of oils and fats are triglycerides, which are triesters of glycerol with three fatty acids. In the triglyceride model shown in Figure 4.4, R1, R2 and R3 represent the three alkyl chains of the fatty acids. It is the variation in the amounts of each fatty acid, their position within the triglycerides and in particular the number and the position of cis double bonds they possess that determine the differences in chemical and physical properties between oils and fats.

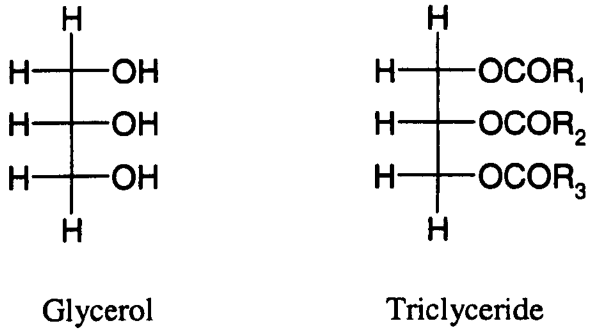

Figure 4.4: Glycerol and triglyceride formula

Fatty acids are essentially straight hydrocarbon chains with a single acid group attached to one end. These chains may or may not contain any double bonds. Most natural fatty acids have an even number of carbon atoms in their chain and are systematically named depending on the number of double bonds and the relative position of the double bonds. However they have also trivial names, which are usually derived from the major source of the acids. They are described by a shorthand system in which the number of carbon atoms follows the letter C, and the number of cis double bonds is placed after a colon following this number. Thus linoleic acid which has 18 carbon atoms in the chain and two double bonds is written C18:2. Table 4.1 gives the name of some common fatty acids along with their nomenclature.

Name of fatty acid	Nomenclature
Butyric	C4:0
Caproic	C6:0
Caprylic	C8:0
Capric	C10:0
Lauric	C12:0
Myristic	C14:0
Palmitic	C16:0
Stearic	C18:0
Oleic	C18:1
Linoleic	C18:2
Linolenic	C18:3
Arachidic	C20:0

Table 4.1: Some fatty acid and their nomenclature[27]

In cocoa butter, there are three main acids which account for over 95% of those present. Almost 65% is oleic acid, about 34% is stearic acid and approximately 26% is palmitic acid. These fatty acids are present in the form of triglycerides. A shorthand notation consisting of three letters is commonly used to describe triglycerides. POSt, for example, has palmitic acid and stearic acid in the outside or 1,3 positions and oleic acid in the middle or 2 position.

About 80% of cocoa butter is in the form SOS where S refers to any saturated fatty acid. Between 1 and 2% of cocoa butter is all saturated (SSS) and melts at a much higher temperature than the more common SOS. From 5 to almost 20% on the other hand contain two oleic acid molecules and are SOO, which is mainly liquid at room temperature. When these are combined, as they are in cocoa butter, the fat will therefore be partly liquid at room temperature. The composition of cocoa butter is influenced by climatic conditions.[28] Table 4.2 shows the typical triglycerides composition of different cocoa butters.[29] There is much interest today in replacing some of the cocoa butter used in chocolate production by mixtures of various vegetable fats (often modified) for technological and economic reasons.[30]

Country of origin	Ivory Coast	Ecuador	Nigeria
POL	0.6	0.7	0.8
MOO, MMP	0.2	0.3	0.2
PPL	1.9	1.9	1.9
OOO	0.8	0.8	0.4
StOL	0.9	0.8	0.8
POO	4.4	3.5	3.2
PStL	3.6	2.8	3.4
PPO	15.9	15.3	14.8
StOO, PPP	6.0	4.8	5.1
StStL	1.8	1.5	1.9
PStO	36.6	3.3	37.4
OOA	1.0	1.2	1.2
PPSt	0.4	0.3	0.7
StStO	23.8	26.9	26.4
StStP	0.8	0.9	0.4
StOA	1.6	2.1	1.9

Table 4.2: Triglycerides composition (%) of cocoa butter[29]

4.2.1.4. Milk products[21]

The majority of cow's milk is water but moisture destroys the flow properties of liquid chocolate so only the anhydrous components can be used. The largest component of dehydrated milk is lactose, the second is milk fat. The later is almost entirely liquid at room temperature so there is a limit to the amount that can be added to chocolate for it to remain hard. The most common powders used for chocolate are skimmed milk and full cream powder.

4.2.1.5. Emulsifier

The most popular emulsifier is lecithin, used to reduce viscosity and save cocoa butter.[22] Soya lecithin is a mixture of phospholipids with other substances such as soya oil.

4.2.2. Chocolate processes

Figure 4.5 shows the essential steps in the manufacture of dark and milk chocolate.

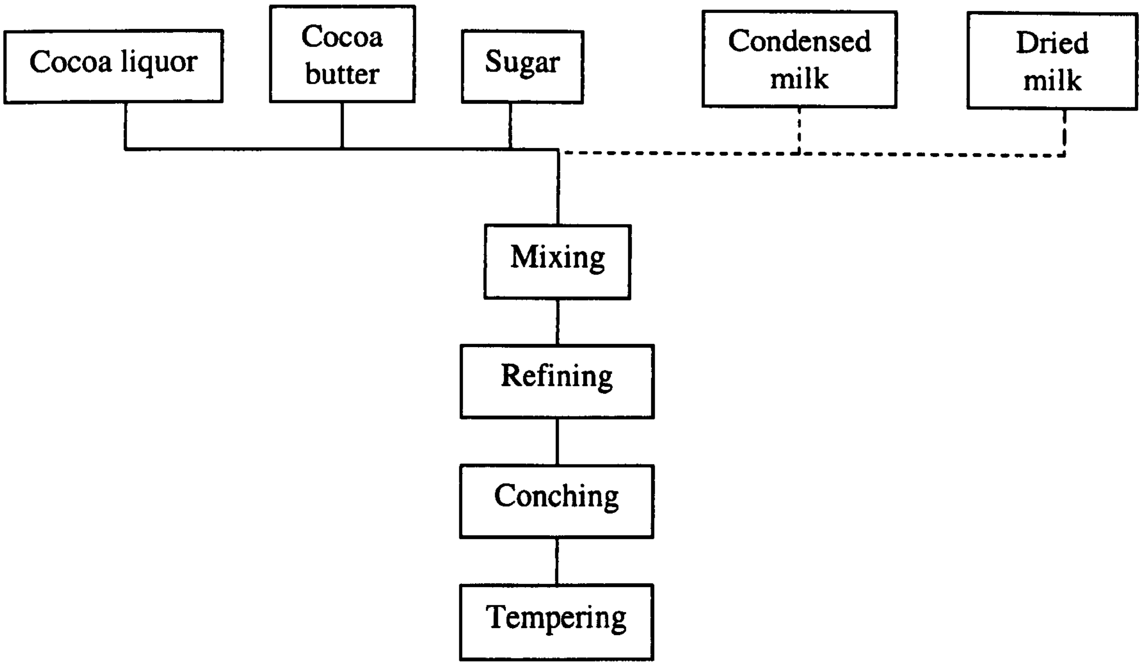

Figure 4.5: Flow sheet of chocolate manufacture[22]

4.2.2.1. Mixing[24]

The sugar, cocoa butter and cocoa liquor used in chocolate manufacture are brought together in a melangeur or similar equipment designed to produce a homogeneous chocolate mix. A melangeur of traditional design consists of two vertically positioned rotating heavy rollers standing on a hardened horizontal, heated bed. The mixing is carried out at 50-60°C. During the mixing process, there is little effect on the size of the cocoa particles but some breakdown of sugar crystals will occur. A better quality chocolate will be produced if the added sugar has been previously milled.[21] The mixing prior to refining should produce a chocolate paste of a somewhat rough texture and plastic consistency. If the texture is too slack, the paste will not climb the rolls of the refiner correctly. If it is too stiff, the passage between the rolls will be retarded or erratic.

With any given formulation, the consistency is obtained initially by experiment, after which a standard recipe can be established for the mixing process.

4.2.2.2. Refining[22]

The refining of chocolate is an important operation and produces the smooth texture which is desirable in modern chocolate confectionery.[24] Refining involves the crushing, abrasion, attrition and shearing of cocoa and sugar fragments to produce a product which has the desired particle size. Over refining can be costly, due to the small sized particles taking excessive amounts of power. The variable factors in any refining process are the feed rate and the degree of reduction. C.C. Hinton[31] has claimed that the limit for the detection of particles by the tongue is 25 microns. Chocolate is usually composed of a mixture of particle sizes which can range from 3 to 100 microns; less than 10% of particles in well refined chocolate lie below 5 microns. Even a small proportion of large particles can produce a gritty effect on the palate. During refining the particle size falls and the total surface area of the particles rises. Increases in the surface area in chocolate particles require the addition of more cocoa butter to maintain the same flow properties. Comparison between chocolate samples with similar compositions show that the smaller the particle size, the greater the viscosity. It follows that an increase in the amount of refining will inevitably change the behaviour of the chocolate in the later stages of processing. It is only during the refining that any significant reduction in particle size occurs. A small reduction in the size of the sugar crystals takes place during mixing but very little, if any change occurs during conching. Chocolate for the UK and the USA markets should be refined to an average particle size of between 20 to 30 microns. Continental tastes demand lower size range of 15-22 microns. A chocolate containing particles of 35 to 40 microns and over in size will find little acceptance among consumers. Conversely, low particle size chocolates, under 15 microns are generally unpleasant to the palate. The most widely used refining equipment is the 3 or 5 roller mill. Each roller operates at different speeds. The feed roll is operated at the lowest speed. The speed of the rolls increases from bottom to top. A low fat chocolate is faster to refine than a high fat chocolate. Processing speeds may therefore be increased by a partial pressing of the mix followed, after refining, by making up with the additional cocoa butter.

A recent development in refining[24] has been the reintroduction of double refining. This uses granulated sugar and avoids the use of sugar mills, which are an explosion hazard.

4.2.2.3. Conching[22]

The process of conching is primarily one of flavour development by removing the undesirable volatile acidic components and by chemical changes that take place in the flavouring components in the chocolate mix. Other secondary effects are: the removal of moisture from the mix; a smoothing of the sharp edges of the sugar crystals; colour changes arising from fat emulsification and from lowering of the fat globule size; changes in viscosity of the mix and thorough mixing which, in particular, breaks up aggregates of sugar and cocoa particles.

Most commercial equipment is designed for a three stage mixing: dry; semi-liquid; liquid. The product from refining is transferred to the conche. Since the paste from the rolls is in a friable and flake form, the required fluidity is only obtained by the addition of extra cocoa butter. Cooling should be given to remove excess frictional heat. Selective additions of more cocoa butter should then be made until the whole recipe weight of fat has been added. At no time should the conche temperature used for milk chocolate rise above 60°C. Many types of conches produce a higher quality product if the cocoa butter is progressively added throughout the process.

The viscosity can be controlled by varying the stage at which cocoa butter is added, and the amount used. As a general rule, a quarter of the lecithin should be added at the start of conching and the remainder towards the end of the conching period. Lecithin in the chocolate during conching reduces the amount of cocoa butter required.[21,22] When the value for moisture falls below 0.7%, no correlation with viscosity has been found.[22] Conching using a reciprocating extruder has been found to reduce the viscosity of chocolate and consume less energy than the usual processes.[32]

The time needed to complete conching has been the subject of considerable debate. Some manufacturers conche for 5 to 7 days to produce a quality product. In milk chocolate comparatively little flavour development occurs through conching, but considerable improvement occurs with dark chocolate.

4.2.2.4. Tempering

Tempering is a method of inducing cocoa butter to crystallise in a stable form in the fluid chocolate mass. This process is necessary to ensure a long shelf-life. Tempered chocolate exhibits better flow properties and have very small crystals of fat.[33] A fault known as bloom can develop.[22] This appears in two forms. The most common one is the development of crystals of unstable fat at the surface of the chocolate and the other is that which arises from sugar crystallisation on the surface of the product (this is not due to bad tempering). Fat bloom formation occurs more readily with plain chocolate than in milk chocolate. This is because of the presence of milk fat and milk phosphatides in the latter.

The state of temper describes the amount of stable fat crystals in the melted chocolate.[21] Cocoa butter has six different crystalline forms. There are two nomenclatures that are used to describe these polymorphs from I to VI or with Greek letters. Table 4.3 shows the temperature ranges at which the different forms crystallise.

Type of crystal		Range of temperature (°C)
γ	I	16-18
α	II	22-24
β_2'	III	24-26
β_1'	IV	26-28
β_2	V	32-34
β_1	VI	34-36

Table 4.3: Nomenclature and temperature of crystallisation of the different forms of cocoa butter[21]

Form V and VI are the most stable. The chocolate maker must ensure that cocoa butter is in form V when it is used to make confectionery products. This form gives a glossy appearance with a relatively good resistance to bloom. Form VI is, in fact, the more stable but under normal conditions it is only formed by a solid to solid transformation and not directly from liquid cocoa butter.

Tempering is therefore a method of achieving the crystallisation of cocoa butter in the stable V form. All the indications are that fat bloom is composed of other crystalline forms of cocoa butter held near or on the surface of the chocolate. During tempering there is a slow crystallisation of cocoa butter in the V form.

Chocolate should first be heated to 48.8°C in a holding kettle. At this temperature all the cocoa butter will become liquid; no further treatment should be undertaken until the chocolate has melted. The melted chocolate should now be cooled to 26.6°C where both stable and unstable forms of fat are crystallised. On reheating to 31-32°C all the unstable crystals will remelt, leaving stable cocoa butter crystals to act as seeds. An improvement in the tempering stage has been found by using a high shear crystalliser which reduces the residence time and the outlet temperature of chocolate.[34]

4.2.3. Fat migration

During the storage of chocolate coated items, the milk fat content of the covering will fall due to the migration of the fat into the centre. The soft fat from different centres also migrates during storage but in the opposite direction thereby changing the fat composition of the chocolate coverture and making it bloom.[22]

In this second case, the lipids most likely to migrate are those with the lowest melting point and greatest fluidity.[35] It is usually the nut centres that bloom first.[21] Nut like hazelnuts contain a fat that is almost all liquid at room temperature. The highly mobile liquid lipids from the filling migrate into the adjacent chocolate resulting in a hardening of the filling and a softening of the chocolate.[36] The softening is increased when the foreign fats are incompatible with cocoa butter. They form a eutectic mixture that dissolves some solid cocoa butter into the liquid phase.[37,38] The eutectic mixture then migrates to the surface of the chocolate where the cocoa butter re-crystallises as bloom.[39,40] A phase diagram can be used to predict the amount of solid fat content present due to migration,[41] which assists the modelling of migration behaviour. Nevertheless, most oils and fats contain more than two TAG's and it is very difficult to study the phase behaviour of these complex multicomponent systems.[42]

The washer test is used to study fat migration.[43] The apparatus consists of a steel washer which is filled with one of the fat-containing components under evaluation. After filling the washer and carefully levelling off the surface, a second washer is glued directly on top of the first. The second washer is filled with the second fat-containing component and the surface is carefully levelled. The sample is then stored at a controlled temperature for a predetermined time. A sample can be removed at different times and analysed for the extent of migration. It should be noted that the sample is destroyed when the analysis is undertaken. Thus, each analysis is completed on a different sample.

The analytical techniques normally used to measure the extent of lipid migration are Nuclear Magnetic Resonance (NMR), DSC,[44] Gas Chromatography (GC)[45,46] or High Performance Liquid Chromatography (HPLC).[47] Magnetic Resonance Imaging has also been used as a non-invasive method.[48,49]

Smith[50] has listed the various factors affecting fat migration as follows:

- Concentration gradient between the triacylglycerols
- Contact area between the chocolate and filling
- Fat level and non-fat solid particles
- Storage temperature[51-53]
- Solid fat content
- Ratio of chocolate to filling
- Fat type
- Chocolate viscosity
- Particle size.

To reduce this type of bloom, anti-bloom fats are usually added to the chocolate or to the centre.[54-56] Another solution is the use of edible barriers.[57]

4.2.4. Chocolate bloom[58]

There are two types of chocolate bloom. Fat bloom arising from changes in the fat in the chocolate and sugar bloom formed by the action of moisture on the sugar ingredients. Although this bloom is detrimental to the appearance of the chocolate, it does not harm its eating qualities unless they have been subjected to poor storage conditions.

4.2.4.1. Fat bloom

Fat bloom is recognised as a greyish coating on the surface of either dark or milk chocolate but it is more visible on the former. It is caused by:

- Bad tempering of the chocolate in the stage of the process
- Incorrect cooling methods, including covering cold centres
- The presence of soft fat in the centres of chocolate covered units
- Warm storage conditions
- The addition to chocolate of fats incompatible with cocoa butter
- Abrasion and finger marking, particularly under warm conditions.

4.2.4.2. Sugar bloom

Sugar bloom has a greyish appearance and in more severe cases it has a crystalline appearance. It is cause by:

- Storage of chocolate in damp conditions or against damp walls
- Deposit of dew during manufacture from damp cooler air or allowing chocolates to enter a packing room at a temperature below the dew point of that room
- Use of hygroscopic ingredients (low grade or brown sugar)
- Removal of chocolate from cold storage without adequate wrapping protection
- Use of damp packing material
- High temperature storage conditions of chocolate covered confectionery where centres have a high equilibrium relative humidity and the water given off is trapped in impervious wrapping.

4.2.5. Viscosity of chocolate

Viscosity is defined as the ratio of shear stress to shear rate. The unit of viscosity is Pascal second (Pa.s).[21]

Chocolate consists of finely ground sugar and cocoa solids dispersed in cocoa butter. Because of the presence of these solids, chocolate does not behave as a true liquid but exhibits non-Newtonian properties.[59] Melted chocolate is a plastic material and flows only when a stress greater than a limiting value acts on it. This limiting stress is termed the yield value. The viscosity of the chocolate will then decrease with increasing shear rate. The plastic properties of melted chocolate are of considerable importance industrially, because chocolate is often deposited into moulds or used with coated centres. If the chocolate is too thick, air bubbles will not easily be removed by the shacking equipment, and the chocolate coating becomes too thick. If the chocolate is too thin, the coating will be to thin, and the chocolates will develop poor decorative marking. The first experiments on chocolate were conducted with a capillary viscometer which was not particularly suitable. About 1950, a concentric cylinder viscometer was used and it was found that the T-D relationship was roughly a straight line, but the curve did not pass through the origin. Better results were obtained by using the Casson equation which was initially used to deal with the rheology of flocculated particles. The equation states that

$$\sqrt{T}-\sqrt{T_0} = \sqrt{\eta_p}\,\sqrt{D}$$

where T is the shear stress, T_0 the yield value, η_p the plastic viscosity and D is the shear rate.

The line is reasonably straight and its slope gives the plastic viscosity which relates to the energy required to keep the chocolate moving once it has started to flow. The intercept on the stress axes determines the yield value which is related to the energy required to start the chocolate moving. Recently, experiments showed that the apparent viscosity of molten chocolate depends not only on the rate of shear but also on its duration and the chocolate does not recover its original viscosity after stirring.

4.2.5.1. Effect of particle size on viscosity[21]

The particle size distribution can take several forms. The two most common are the number *vs.* size distribution and the mass *vs.* size distribution.

In chocolate a small number of larger particles will give a gritty texture. Therefore, the number distribution will not give the information that is needed. The mass distribution is better and usually the 90th percentile is taken. It is the size at which 90% of the particle mass is due to particles with a diameter less than this size. This value appears to correlate fairly well with what people actually taste.

The largest particle size is important for mouth-feel with respect to grittiness, but the smaller particles are more important with respect to chocolate flow properties, in particular the yield value. For the same recipe, a chocolate containing a larger amount of small particles will be more viscous than one containing larger particles. This is due to the large amount of fat required to coat them.

4.2.5.2. Effect of moisture content on viscosity[21]

Chocolate normally contains 0.5 to 1.5% of moisture and if further minute amounts are added and mixed in as free moisture, the viscosity greatly increases. If the same amount of water is added to the liquid fat alone, no similar viscosity change occurs but with a fine sugar and fat mixture, the viscosity is the same as with chocolate. Moisture at the surface of the sugar particles increases the friction between them. This results in a greater resistance when the particles move among themselves and produce the effect of increasing the viscosity.[60] The addition of 3 or 4% by weight of water will turn chocolate into a very thick paste. Roughly for 0.3% extra moisture that is left within the chocolate at the end of conching, the manufacturer must add an extra 1% of fat. Because the fat is by far the most expensive major component of chocolate, it is important that as much free water is removed as possible.

4.2.5.3. Effect of fat on viscosity[21]

Addition of fat helps a chocolate to flow more easily. Most chocolates contain between 25-35 % fat. Above a fat content of 32% there is very little change in viscosity with any further addition. The effect of fat is proportionately much higher for the plastic viscosity than the yield value.

4.2.5.4. Effect of lecithin on viscosity

Lecithin displays both hydrophilic and lipophilic properties.[24] When lecithin is added, the hydrophilic groups of the molecules attach themselves firmly to the water molecules on the surface of the sugar particles. This reduces friction, increases particle mobility and lowers viscosity. The addition of 0.1% to 0.3% lecithin is said to reduce the viscosity by more than 10 times its own weight of cocoa butter.[21] Too much lecithin, however can be detrimental to flow properties. At 0.5%, the yield value increases with increase in lecithin addition, although usually the plastic viscosity continues to fall.

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CHAPTER V

CO-CRYSTALLISATION SUCROSE-HONEY

5.1. Aim

Co-crystallisation of carbohydrates has been associated with glucose and fructose together or separately in a matrix of sucrose crystals. The co-crystallisation of honey with sucrose has already been studied (Bhandari *et al.*, 1998)[1] and the stability of honey flavour was evaluated. Nevertheless, the crystallisation of individual sugars during the co-crystallisation process was not investigated.

In a more recent paper, sucrose was co-crystallised in the presence of pure glucose and fructose either separately or together (Bhandari and Hartel, 2002)[2]. It was reported that no crystallisation of fructose or glucose occurred during the co-crystallisation process although crystallisation of glucose in the monohydrate form was observed during storage in the samples only involving sucrose and glucose.

In the present work, the co-crystallisation of sucrose with honey was studied, focusing on the solid state of the different sugar components of the materials and looking at the influence of the amount of honey and the type of honey added (clear or granulated).

5.2. Observation of the materials

The co-crystalline products were prepared following Method 9.2. When the product had not been filtered the amount of honey added had a profound effect on the consistency of the material. With honey (ca. 11.1 g) added to sucrose syrup (100 g) the product was dry and after grinding, a powder was obtained. On increasing the amount of honey (Table 5.1), the product was stickier and the grinding resulted in larger agglomerates. When centrifugal filtration was used the amount of honey added had no influence on the consistency of the co-crystallised product and in each case a dry powder was obtained.

Method	Amount (g) of honey added to 100 g of sucrose	Consistency/appearance	
		Before drying or filtration	After drying or filtration
Without filtration	7.00	Almost dry	Dry powder
	13.52	Soft-creamy	Sticky agglomerates
	24.23	Creamy	Very sticky chunks
With filtration	12.21	Almost dry	Dry powder
	19.19	Soft-creamy	Dry powder
	24.20	Creamy	Dry powder

Table 5.1: Consistency and appearance of the co-crystallised products obtained from sucrose and honey

These visual observations were confirmed by Scanning Electron Microscopy. When the products were filtered (Figure 5.2), the photomicrographs showed the micro-size sugar crystals agglomerated together whereas the non-filtered products, especially those that contained high amounts of honey, showed a film of material coating the sucrose crystals (Figure 5.1).

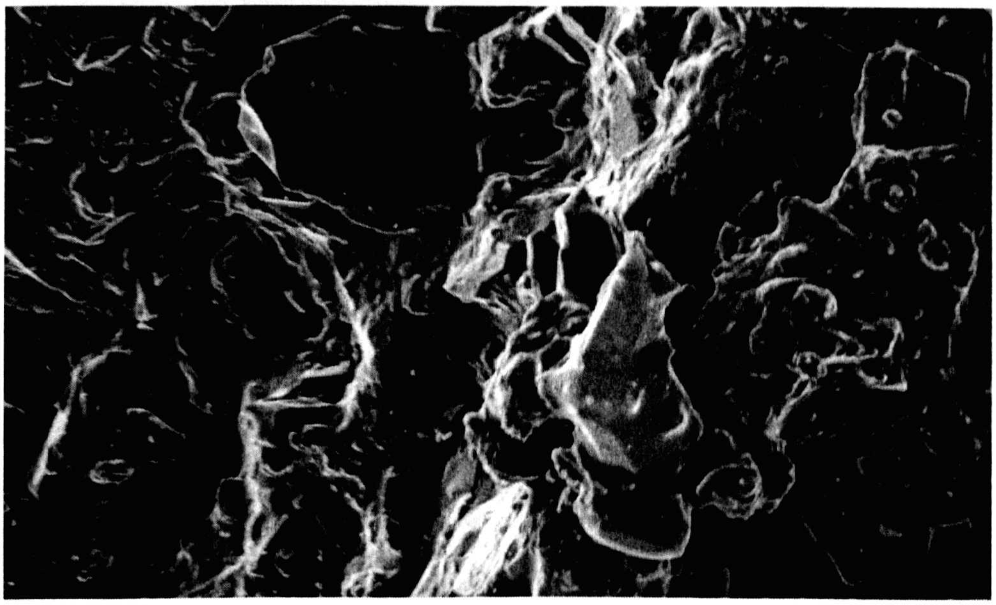

Figure 5.1: Photomicrograph of a co-crystalline sucrose-honey product non-filtered (20% of honey added)

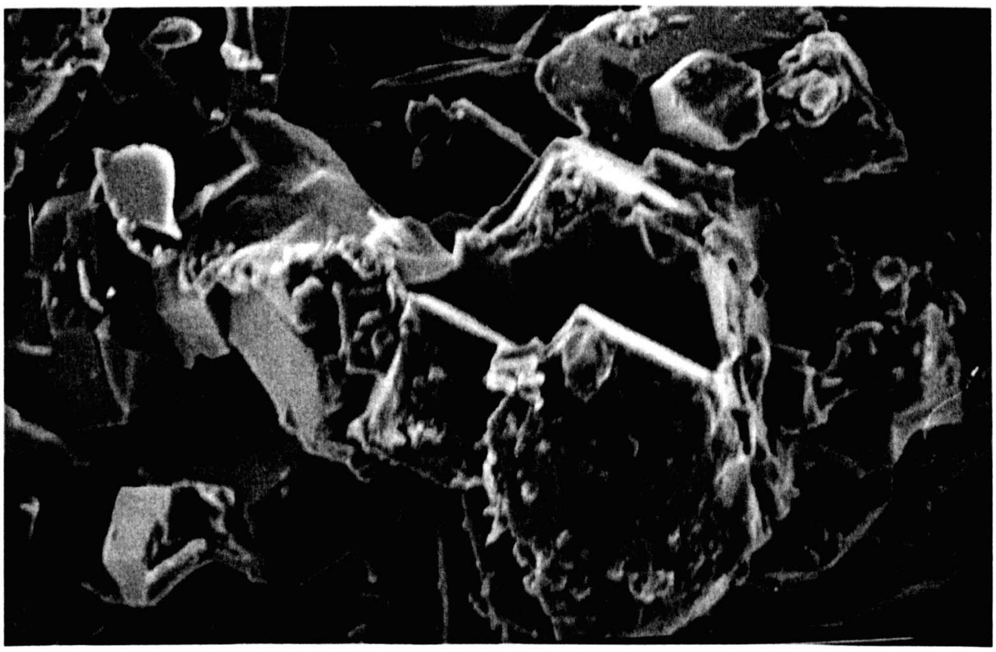

Figure 5.2: Photomicrograph of a co-crystalline sucrose-honey product filtered (20% of honey added)

5.3. Composition of the granules

The composition of the granules, obtained by centrifugal filtration, found by integration of the peaks obtained by HPLC for sucrose, fructose and glucose is shown in Table 5.2 This table also shows analytical data for the sugars present in the mother liquor removed by centrifugal filtration. Both the "Australian Eucalyptus Clear Honey" and the "Set Honey" (granulated honey) have a larger content of fructose compared to glucose which is the case for most honeys (White, 1975)[3]. This difference is greater for the Set Honey (ratio glucose/fructose of 0.8) than for the Australian Honey (ratio glucose/fructose of 0.6). The amount of mother liquor removed by centrifugation increases with the amount of honey added for both the Set and the Australian honeys. Indeed the addition of honey increased the level of water (honeys are composed on average of 17% of moisture)[3] and impurities in the sucrose solution. Although fructose and glucose decrease the solubility of sucrose their influence on slowing the nucleation process of sucrose and crystal growth is far higher. Furthermore, the overall solubility of the three sugars together is increased.

Type of honey	Proportion of Honey added	% of mother liquor	Proportion of the sugars in the crystals		
			Fructose % by weight	Glucose % by weight	Sucrose % by weight
Australian Honey	10%	15	0.27 (±0.10)	0.32 (±0.1)	99.41 (±0.1)
	15%	22	0.69 (±0.05)	0.71 (±0.05)	98.60 (±0.05)
	20%	25	1.24 (±0.05)	1.13 (±0.05)	97.63 (±0.05)
Set Honey	10%	17	0.67 (±0.05)	0.71 (±0.05)	98.70 (±0.05)
	15%	23	0.63 (±0.05)	0.74 (±0.05)	98.63 (±0.05)
	20%	25	0.92 (±0.05)	1.01 (±0.05)	98.07 (±0.05)

Table 5.2: Percentage of filtrate and composition of the granules obtained after centrifugation

The proportion of glucose and fructose remaining in the granules obtained by filtration increased with the amount of honey added but remained very low in relation to the amount of sucrose. The proportion of combined fructose and glucose is 2% of the sugars present in the co-crystalline mixtures for 20% of honey added to the sucrose. This result proves that the major part of glucose and fructose remained in an amorphous form at the end of the co-crystallisation process and were not completely incorporated into the sucrose matrix. At 10% of honey added the proportion of fructose and glucose remaining was higher for the Set honey than for the Australian honey, but the trend was reversed at 20% of honey added. However, the differences between both honey ingredients appear not to be significant in relation to the composition of the co-crystalline materials prepared.

5.4. Influence of the amount of honey added on the physical properties of the products

5.4.1. Moisture content

Proportion of honey added	Set Honey		Australian Honey	
	Centrifuged	Non-centrifuged	Centrifuged	Non-centrifuged
10%	1.2	2.2	1.2	1.3
15%	1.2	2.3	1.5	2.0
20%	1.3	3.3	2.4	4.7

Table 5.3: Moisture content of the agglomerates

The average moisture content obtained for duplicate assays for the co-crystalline products is shown in Table 5.3. As expected the moisture level increased with the amount of honey added and that which is adsorbed. This result was seen by visual observation in that the agglomerates were softer and the crystallisation was slower at high levels of honey added. An increase in moisture content was also observed in the products from which the mother liquor was removed showing that the level of moisture follows the amount of glucose and fructose present in the product. Both glucose and fructose probably remained in the amorphous form thus increasing the hygroscopicity of the mixture. Indeed the amorphous form of the sugars has a strong tendency to take up water vapour. This tendency is much greater than that of the corresponding crystalline forms.[4]

5.4.2. Flowability of the products

Proportion of honey added	Set Honey		Australian Honey	
	Centrifuged	Non-centrifuged	Centrifuged	Non-centrifuged
10%	37.5 (0.5)	37.0 (1.0)	38.0 (0.5)	36.5 (0.5)
15%	38.0 (0.5)	38.5 (0.5)	39.0 (1.0)	38.0 (0.5)
20%	38.5 (0.5)	39.5 (1.0)	40.0 (1.0)	39.0 (0.5)

Table 5.4: Angle of repose of the agglomerates. The standard deviation is in brackets

The flowability measurements shown in Table 5.4 are average on four replicates. As expected, an increase in the proportion of honey present in the granules of the co-crystalline materials had a significant effect on flowability. Thus, the flowability was found to decrease (increase of the angle of repose) with increase level in honey present. The trend is in parallel with that found for the centrifuged products, though to a lesser extent. The flowability of a powder is linked to its moisture content. Food powders exposed to high relative humidity have often poor flowability properties.[5]

5.4.3. Melting characteristics

DSC traces are shown in Figures 5.6, 5.7, 5.8 and 5.9 and the corresponding data are recorded in Tables 5.5 and 5.6. All the traces showed a similar melting behaviour with a two-peak pattern for sucrose: a minor peak around 150°C (Tp1) and a second one around 180°C (Tp2). The first peak of the two-peak pattern cannot be explained by the presence of either fructose or glucose in the crystalline form since it is present when the co-crystallisation process was applied to sucrose alone (Figure 5.11). Our work on this feature will be detailed in Chapter 7. None of the DSC scan showed the melting peak for fructose, anhydrous glucose or glucose monohydrate which melt at 120°C, 145°C and 80°C respectively.

Type of Honey	% of honey added	Tg (°C)	ΔCp (J/g°C)	Tp1 (°C)	ΔH1 (J/g)	ΔH2 (J/g)	Tp2 (°C)	ΔH_{Total} (J/g)
Set Honey	10	45.5 (±2.1)	0.8 (±0.2)	150.8 (±0.1)	10.5 ((±1.2)	75.5 (±3.1)	179.1 (±0.5)	86.0 (±4.3)
	15	32.6 (±2.2)	0.7 (±0.1)	151.3 (±0.1)	8.9 (±1.0))	62.1 (±2.2)	176.8 (±0.5)	71.0 (±3.3)
	20	36.7 (±2.1)	0.8 (±0.2)	151.1 (±0.1)	7.9 (±0.5)	59.0 (±2.0)	173.3 (±0.1)	66.9 (±2.5)
Austr. Honey	10	27.0 (±2.3)	0.3 (±0.1)	151.0 (±0.1)	7.0 (±1.1)	86.5 (±2.4)	179.9 (±0.1)	93.4 (±3.5)
	15	15.3 (±2.1)	0.6 (±0.2)	151.2 (±0.1)	8.2 (±2.2)	70.9 (±3.2)	177.7 (±0.2)	79.1 (±5.4)
	20	39.9 (±3.0)	0.7 (±0.2)	151.4 (±0.1)	9.1 (±1.3)	64.5 (±2.0)	172.8 (±0.1)	73.6 (±3.3)

Table 5.5: DSC results for the co-crystallised products non-filtered

Type of Honey	Proportion of honey added	Tp1 (°C)	Tp2 (°C)	ΔH_{Total} (J/g)
Set Honey	10%	152.4 (±0.3)	182.4 (±0.1)	87.0 (±3.1)
	15%	151.9 (±0.1)	181.9 (±0.2)	86.2 (±1.2)
	20%	151.7 (±0.1)	181.6 (±0.1)	80.3 (±3.3)
Australian Honey	10%	151.1 (±0.1)	182.8 (±0.8)	114.3 (±3.0)
	15%	151.4 (±0.1)	182.0 (±0.5)	110.8 (±3.2)
	20%	151.5 (±0.1)	181.3 (±0.3)	94.2 (±5.0)

Table 5.6: DSC results for the co-crystallised products filtered

When centrifugal filtration was not used, a glass transition appeared which was not observed when the products were filtered. The total enthalpy of melting of sucrose decreased with increase in the level of honey in both the non-filtered and filtered products (Figure 5.3). For the same type of honey and the same amount of honey added, the total enthalpy was found to be higher when the mother liquor was removed. The presence of impurities is known to decrease the amount of energy necessary to melt crystalline sucrose (Roos, 1993).[6]

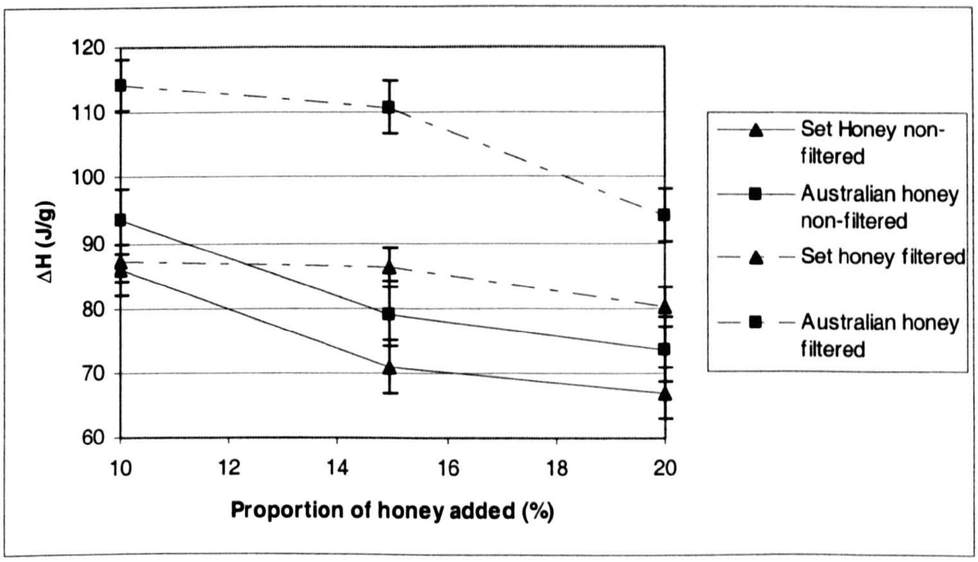

Figure 5.3: Evolution of the total sucrose enthalpy with increase levels of honey

Observation of the enthalpy of each of the peak ($\Delta H1$ and $\Delta H2$) shows that as the amount of honey present is increased, the second peak decreases in enthalpy. In contrast, little change in enthalpy is observed for the first peak. The increase of the level of honey did not seem to have a significant effect on the temperature of the first peak (Figure 5.4), whereas the temperature of the second peak decreased with increase in level of honey especially when the co-crystalline products were not filtered (Figure 5.5).

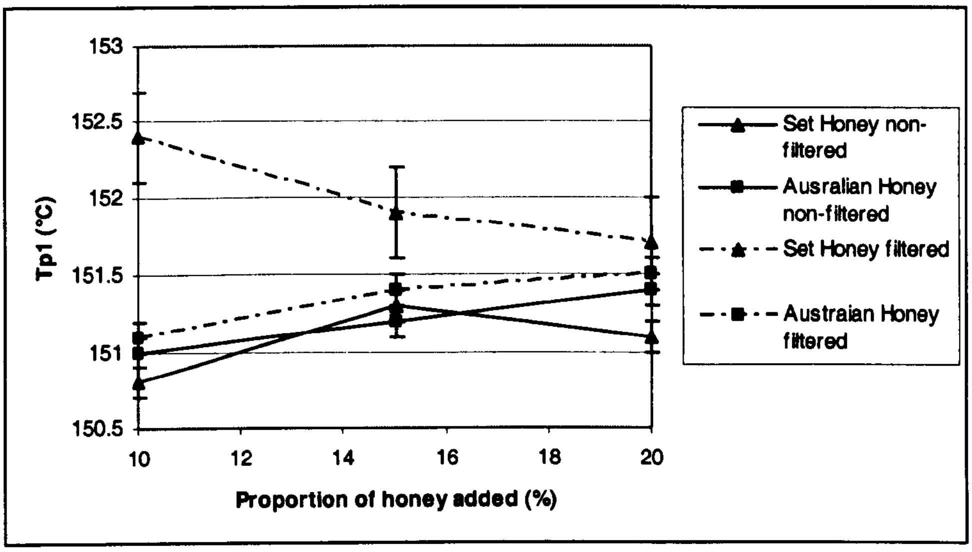

Figure 5.4: Evolution of the temperature of the first melting peak with increase levels of honey

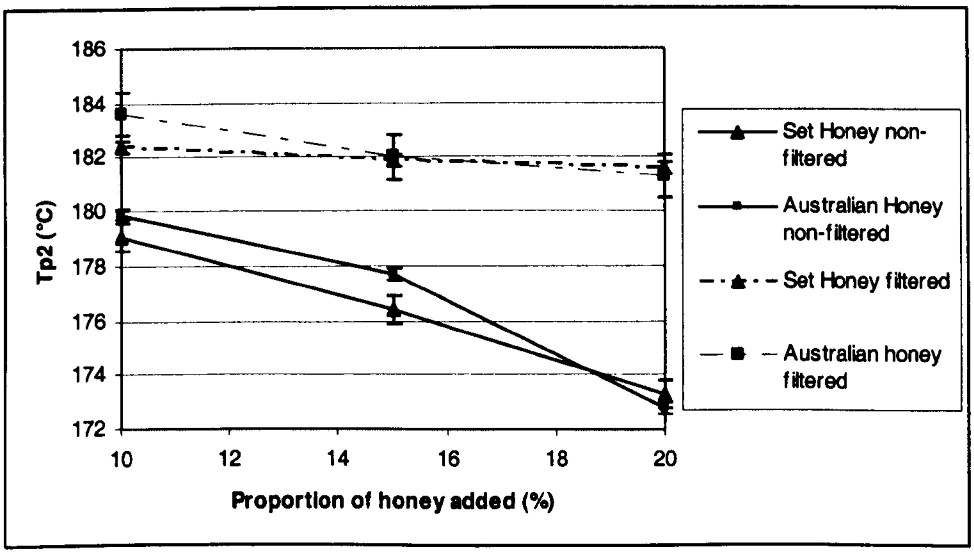

Figure 5.5: Evolution of the temperature of the second melting peak with increase levels of honey

The Tg values of sucrose in the literature vary depending of the method used. They range from 52 to 70°C (Bonelli *et al.*, 1997)[7] for melted sucrose, but it was measured at 74°C (Saleki-Gerhardt and Zografi, 1994)[8] for freeze dried sucrose. The lower values obtained in this study can be explained by the presence of fructose and glucose in the amorphous phase. The reported values for glucose and fructose are, respectively, 31 to 39 and -4 to 13°C (Finegold *et al.*, 1989; Orford *et al.*, 1990; Ablett *et al.*, 1992; Roos, 1993)[9,10,11,6]. Their presence is known to decrease the glass transition temperature of sucrose. The glass transition temperature of a mixture of sucrose and glucose (1:1 by weight) has been reported at 47°C and that of a mixture of sucrose and fructose (1:1 by weight) has been reported at 25°C (Orford *et al.*, 1990)[10]. Furthermore, the impact of residual moisture content of freeze dried sugar matrices on Tg has been investigated (Bonelli *et al.*, 1997)[7]. It was found that the Tg value was increasingly sensitive to the water content of sugars at low water content. In our case, the Tg of the materials reached a minimum at 15% of honey added in the agglomerates (Figure 5.10). This can be explained by fructose and glucose existing in the amorphous phase and a greater moisture content. At 20% of honey added, the transition temperatures are at their highest in this study, though the moisture content for these products was very high. The proportion of non-crystalline sucrose was at its highest for this level of honey added.

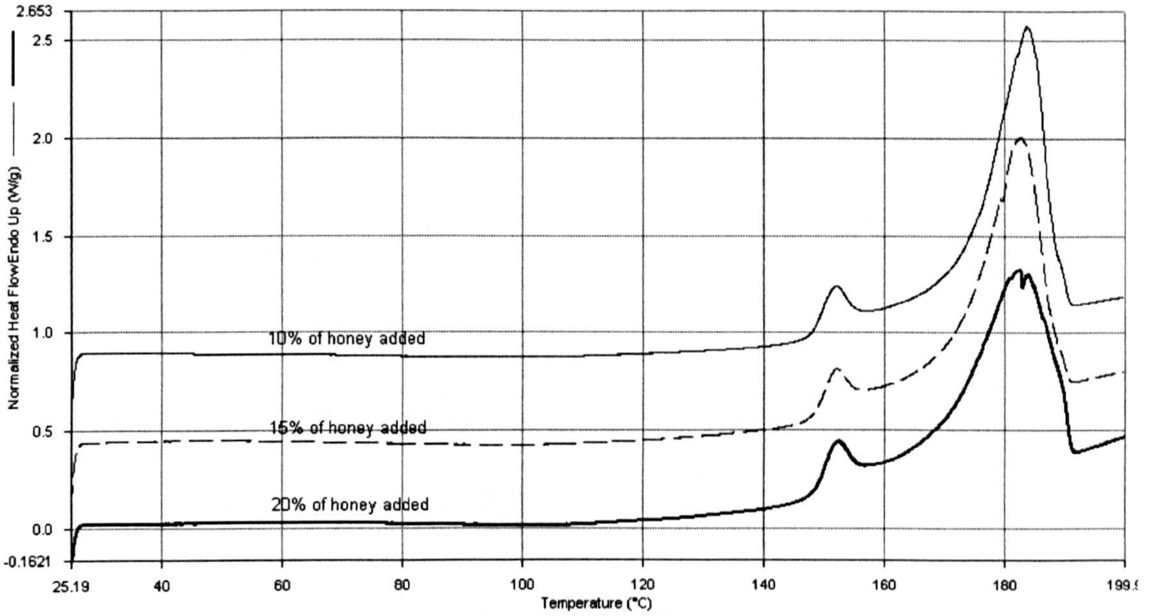

Figure 5.6: Melting endotherms of co-crystallised Sucrose-Australian Honey filtered

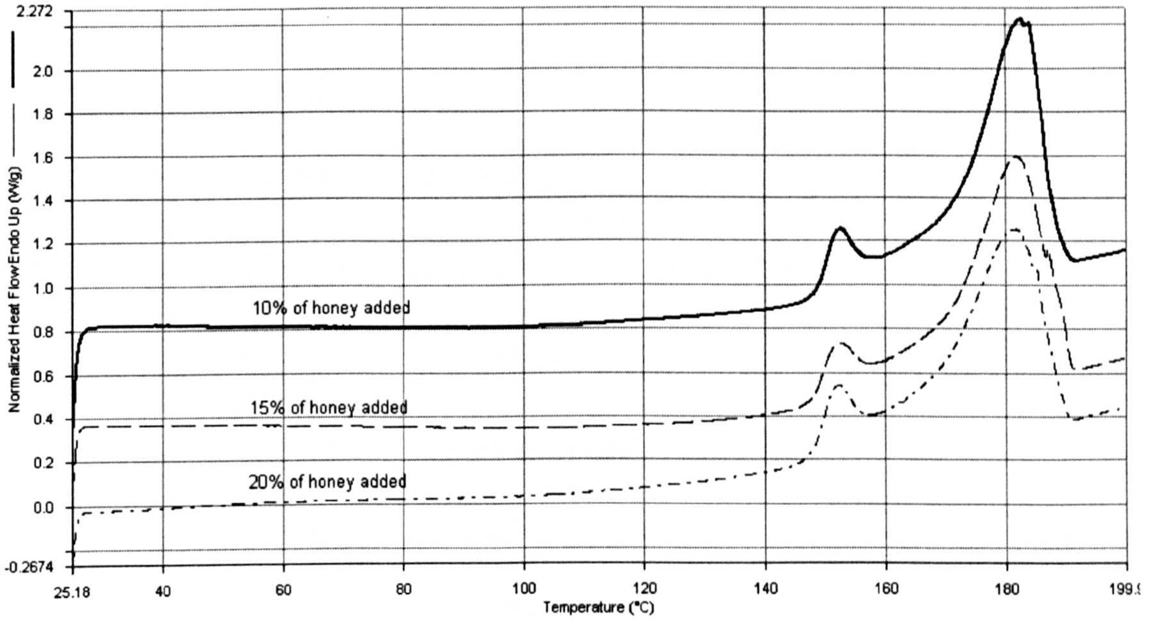

Figure 5.7: Melting endotherms of co-crystallised Sucrose-Set Honey filtered

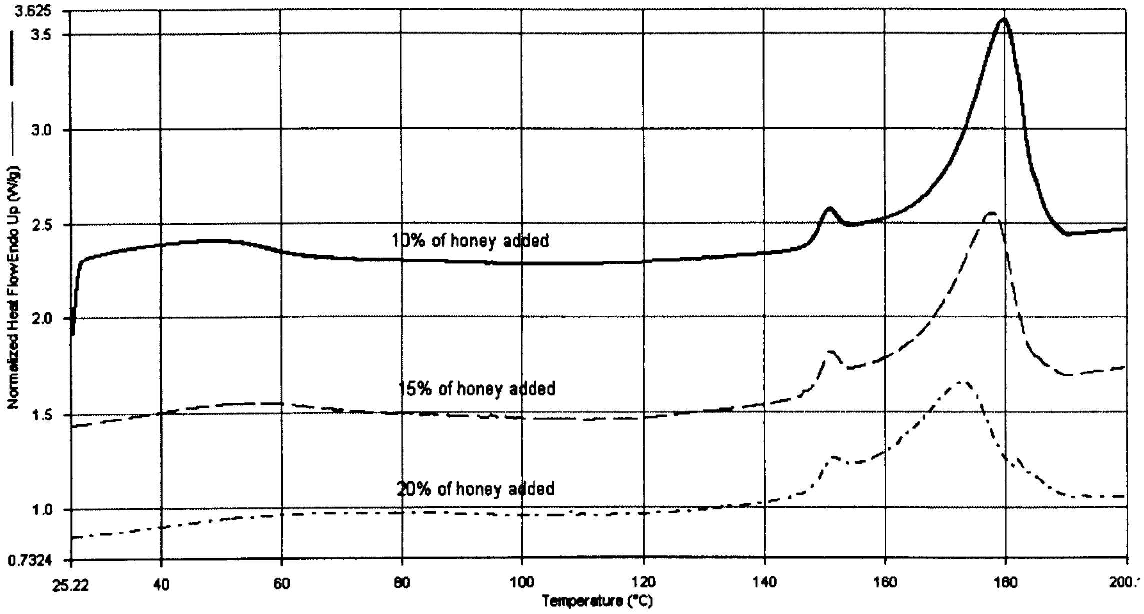

Figure 5.8: Melting endotherms of co-crystallised Sucrose-Australian Honey non-filtered

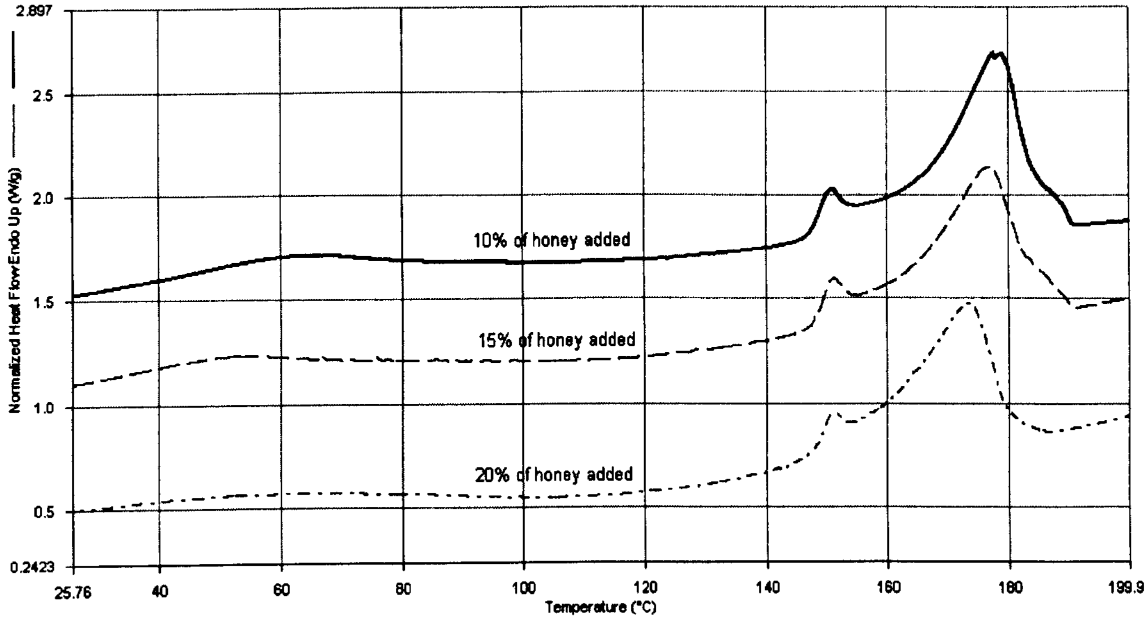

Figure 5.9: Melting endotherms of co-crystallised Sucrose-Set Honey non-filtered

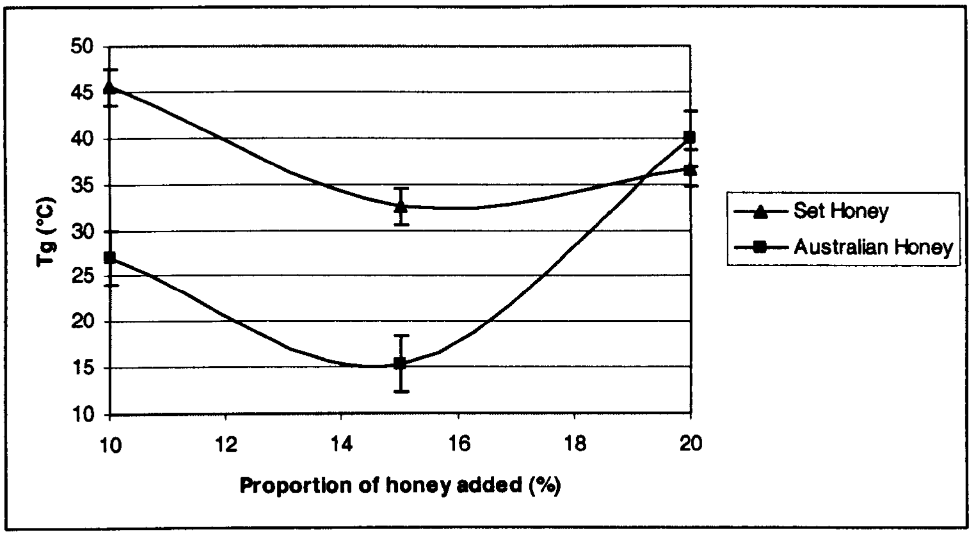

Figure 5.10: Evolution of the temperature of glass transition with increase levels of honey

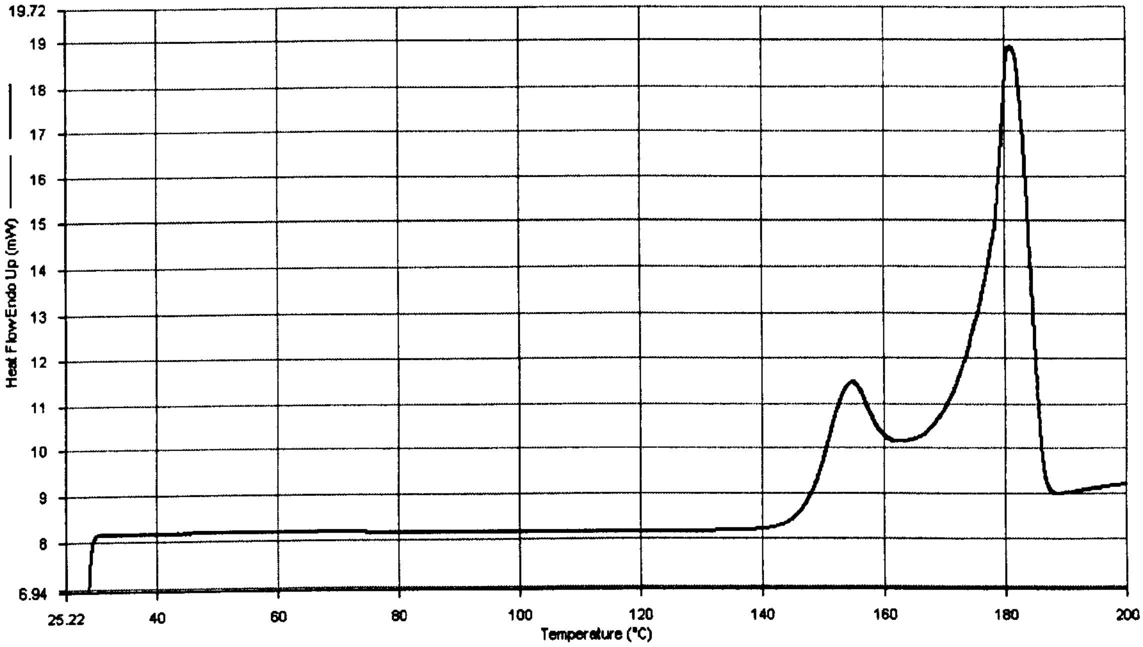

Figure 5.11: DSC trace of re-crystallised sucrose

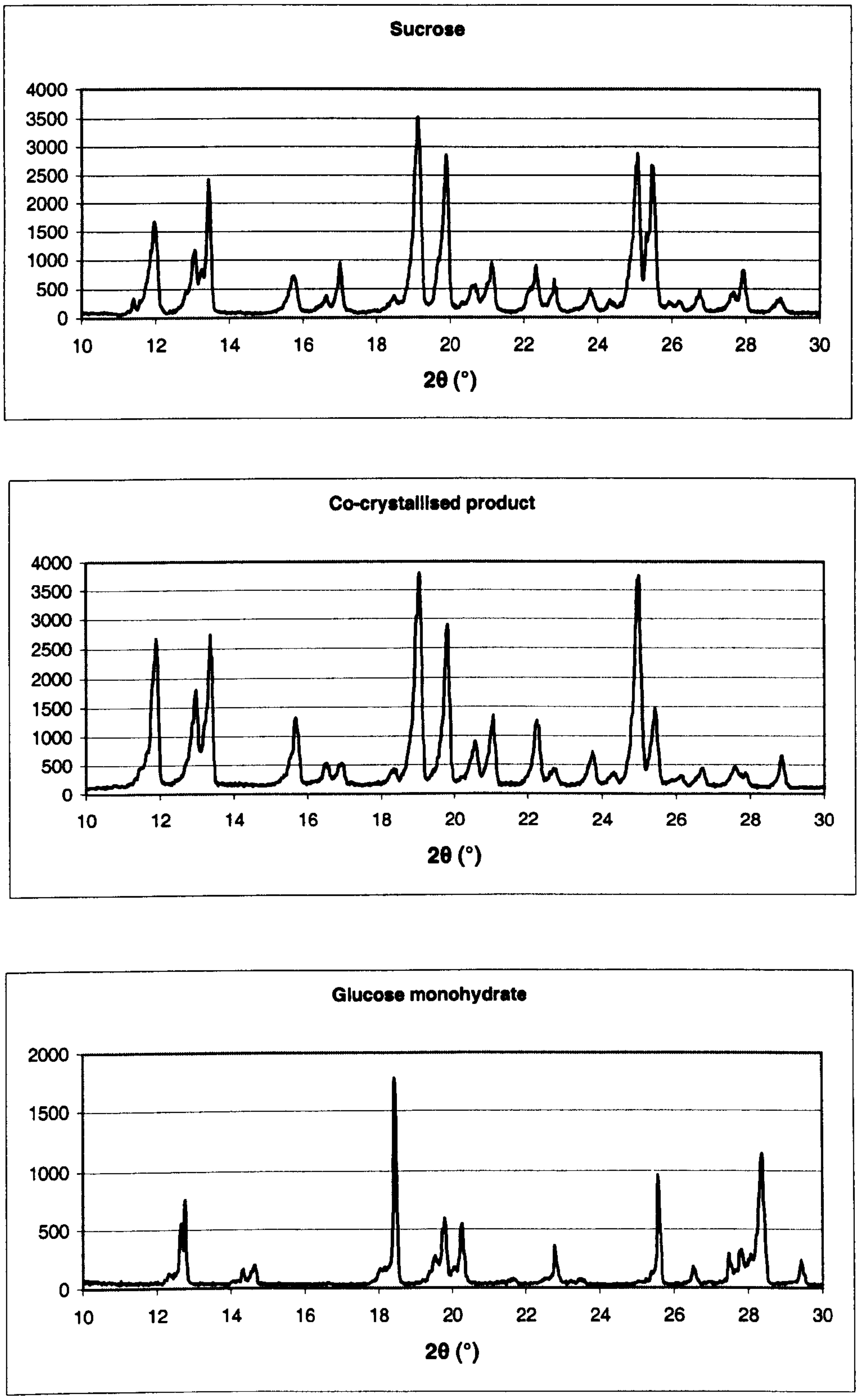

Figure 5.12: X-ray diffraction patterns of sucrose, glucose monohydrate and a co-crystallised product (Sucrose-Clear Honey 9:1)

The X-ray Diffraction patterns of sucrose; the co-crystalline product; glucose monohydrate are shown in Figure 5.12. The pattern of the co-crystalline product was similar to that of sucrose which confirmed the results from the DSC analysis. In any case the presence of glucose monohydrate is very difficult to determine by X-ray analysis. Indeed mixtures of sucrose and glucose monohydrate both in the crystalline form were prepared. The presence of glucose monohydrate present at a proportion of 5% could not be detected by X-ray analysis. The reason for using two different types of honey was to evaluate any differences in crystallisation of fructose and glucose during the co-crystallisation process and upon storage. We can conclude that neither glucose nor fructose crystallised at the end of the co-crystallisation process and this independently of the honey being clear or granulated.

5.5. Evolution of the products after storage

When the same products were analysed by DSC after several month of storage, the melting endotherm of glucose monohydrate appeared on the traces of some of the samples prepared with the granulated honey (four out of twelve filtered as well as non-filtered) (Figure 5.13). Crystalline glucose monohydrate was not found at all on the DSC traces of the products prepared with the clear honey. It was not possible to confirm the presence of crystalline glucose monohydrate by X-ray diffraction analysis. One of the proposed indices to predict the tendency of honey to granulate is the glucose/water ratio (White, 1975)[3]. Though the moisture content in the co-crystallised materials is much lower than in honeys, the tendency of the Set honey to granulate remained. This tendency was however slowed by the co-crystallisation process.

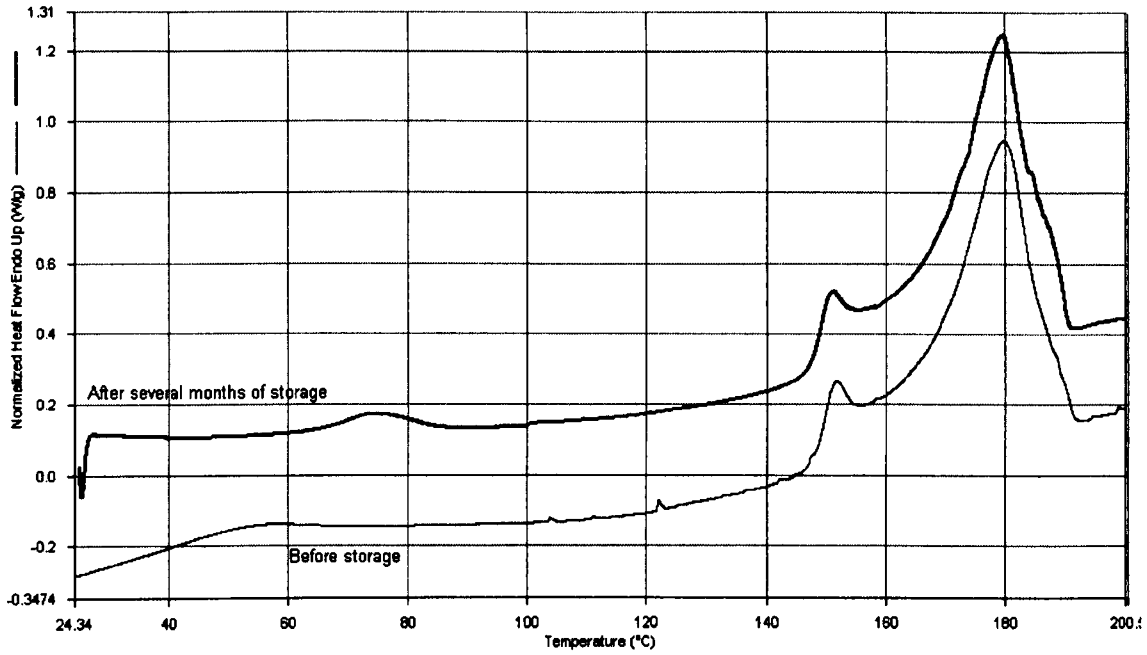

Figure 5.13: DSC traces of a co-crystalline product before and after storage showing crystalline glucose monohydrate

5.6. Conclusion

By removing the mother liquor, only a maximum of 2% of honey sugars was incorporated during the co-crystallisation process. The crystallisation of sucrose was significantly inhibited by the presence of honey. A two-peak pattern was obtained by DSC for the melting endotherm of sucrose at 150 and 180°C. An increase level in honey in the material had a greater effect on the second component of this pattern. The individual monosaccharides of honey did not crystallise during the co-crystallisation process. However, glucose monohydrate crystallised upon storage in some of the products prepared with the partially granulated honey.

5.7. References

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CHAPTER VI

CO-CRYSTALLISATION SUCROSE-GLUCOSE

6.1. Aim

The study of the co-crystallisation of sucrose with honey has shown that the monosaccharides, glucose and fructose, did not crystallise during the co-crystallisation process (Chapter 5). The present chapter focuses on a particular carbohydrate component of honey, namely glucose. The crystalline state of the carbohydrate components of food products is of great importance for such parameters as shelf life and texture. An understanding of the principles that control the crystallisation of the sugars is thus important. The physical properties of glucose and sucrose as pure materials are different. Sucrose crystallises in only one structural known form above 0°C whereas glucose can be prepared in three crystalline forms which are α-D-glucose monohydrate, anhydrous α-D-glucose and anhydrous β-D-glucose. The solubility values of glucose vary according to the type of glucose being examined. At room temperature, glucose is less soluble than sucrose but it becomes more soluble above 50°C.[1] In addition, at any given boiling temperature, the sucrose concentration will be higher than that of glucose.[2] Saturation concentration and boiling point concentration, can be expressed in a single graphical form to permit an overall picture of the properties of supersaturated solutions. Supersaturation is the driving force for crystallisation.[1,2] The rate and quantity of material crystallised are governed by the degree of supersaturation. Much greater supersaturation levels are required for glucose monohydrate to crystallise spontaneously than for sucrose. Furthermore, the properties of a sugar, namely, its solubility and boiling point elevation, are influence by the presence of additional sugars. The effects of glucose on sucrose solubility[2], nucleation[3] and growth[4] have already been studied. For example, mixtures of glucose and sucrose have a greater total solubility than those of glucose and sucrose alone, but individual solubilities are depressed. The aim was thus to investigate the co-crystallisation of sucrose and glucose and characterise the materials prepared for their melting behaviour, crystalline state and flowability. It was intended to study the conditions required to prepare a free-flowing material suitable for use in confectionery. Another objective was to undertake a comparative study of the phase diagrams of sucrose-glucose systems obtained from both physical grinding and the co-crystallisation process.

6.2. Co-crystallisation sucrose-glucose: sucrose as the main ingredient

The co-crystallisation of sucrose with glucose was investigated by varying different parameters: type of glucose; temperature of re-crystallisation; source of sucrose.

6.2.1. Effect of the type of glucose added

Differences of crystallisation behaviour of the sugars have been found during the study of the co-crystallisation of honey with sucrose by using either a clear or granulated honey. As a consequence, in the first instance, the co-crystallisation of sucrose and glucose was carried out using glucose in three different forms: anhydrous α-D-glucose (or dry method), α-D-glucose monohydrate and a concentrated solution of glucose (or wet method) (Method 9.3.1.1). Figure 6.1 shows the amount of filtrate obtained after centrifugal filtration for the three experiments performed and the three proportions used. When anhydrous glucose crystals were added to the concentrated sucrose solution, the more glucose was added the less filtrate was obtained after centrifugal filtration. When glucose monohydrate (which contains about 10% of water by weight) and the concentrated solution of glucose were added, the amount of syrup obtained at 10% proportion was similar to that obtained with anhydrous glucose. However, when 15 and 20% of glucose were added, the percentage by weight of filtrate removed increased for each of the two first methods employed.

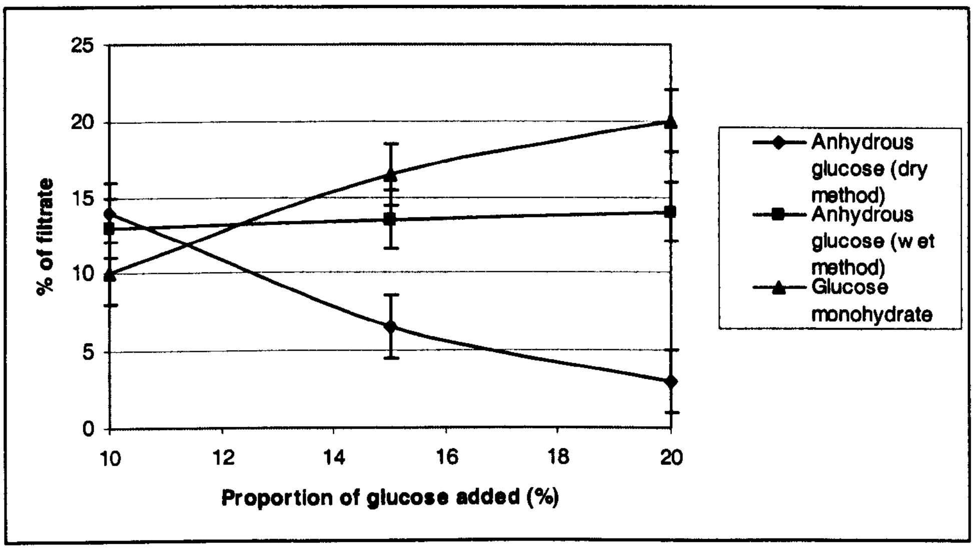


Figure 6.1: Percentage of filtrate obtained from centrifugal filtration for the different proportions of glucose added

This result can be explained by the water carried into the mixtures by glucose monohydrate and the concentrated solution of glucose respectively. Before centrifugal filtration, these two methods gave final products which were very creamy at 20% of glucose added. Furthermore, the water carried into the mixtures dissolved a great quantity of the component sugars. This result is reflected by the contents of the crystals recovered after centrifugal filtration (Figure 6.2). During the co-crystallisation process, when anhydrous glucose crystals were added, the most part of the glucose remained in solution. The trend was even more significant when glucose monohydrate and as might be expected the concentrated glucose solution were used. In contrast, the proportion of glucose in the filtrate was relatively high and increased with an increasing amount of glucose added (Figure 6.3).

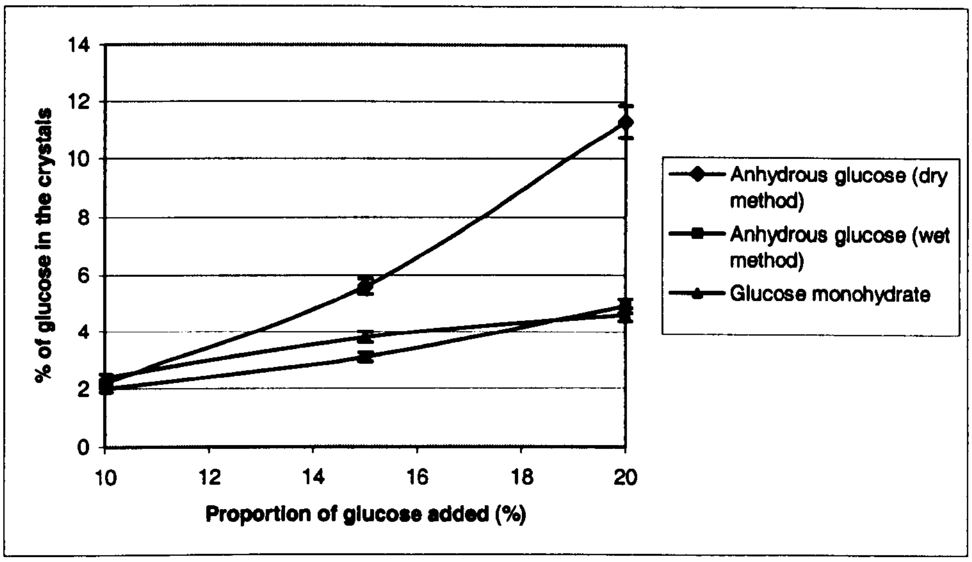


Figure 6.2: Evolution of the percentage of glucose in the solid after centrifugal filtration with increase levels of glucose added

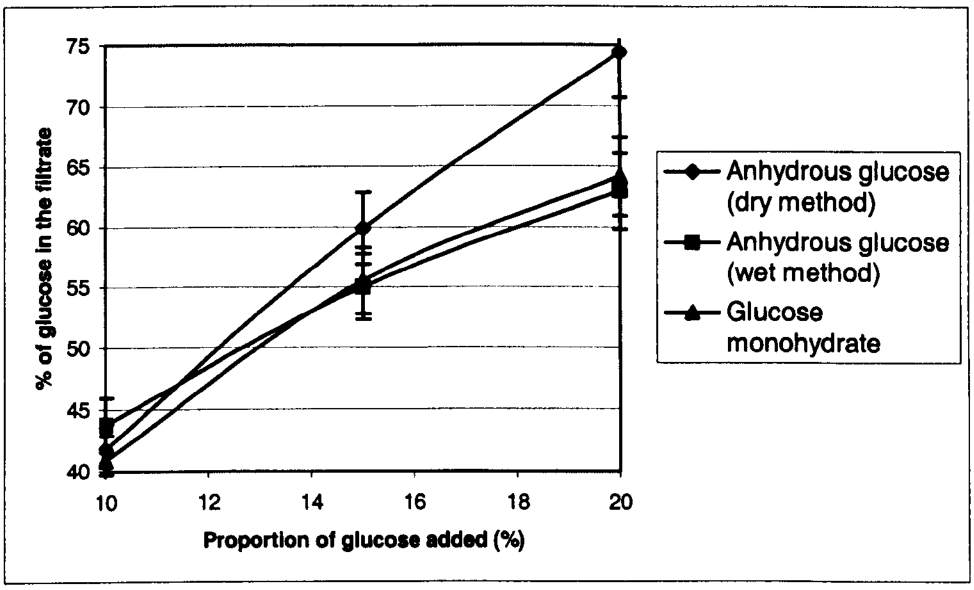


Figure 6.3: Evolution of the percentage of glucose in the filtrate after centrifugal filtration with increase levels of glucose added

The DSC traces and corresponding data obtained for the dry method, the use of glucose monohydrate and the wet method are shown in Figures 6.4, 6.5, 6.6 and Tables 6.1, 6.2 and 6.3 respectively. In the case of the dry method, the DSC traces showed a profile in which the melting endotherms were observed for glucose monohydrate at around 80°C, anhydrous glucose at about 144°C and sucrose at around 180°C appeared. The ΔH for glucose monohydrate increased slightly with increasing levels of glucose added but the most significant evolution was that observed for the enthalpy of anhydrous glucose which increased from 17 to 61 J/g. The melting endotherm for sucrose had a two-peak pattern: a small peak at 150°C (± 2) and a major one around 176°C (± 4). The temperature of the second peak of sucrose decreased with the amount of glucose added. During the co-crystallisation process the main part of the glucose which re-crystallised was in the anhydrous form and increased as cooling proceeded. However, crystallisation of glucose was not complete when the mixture reached 50°C. Below this temperature all remaining glucose crystallised in the monohydrate form.

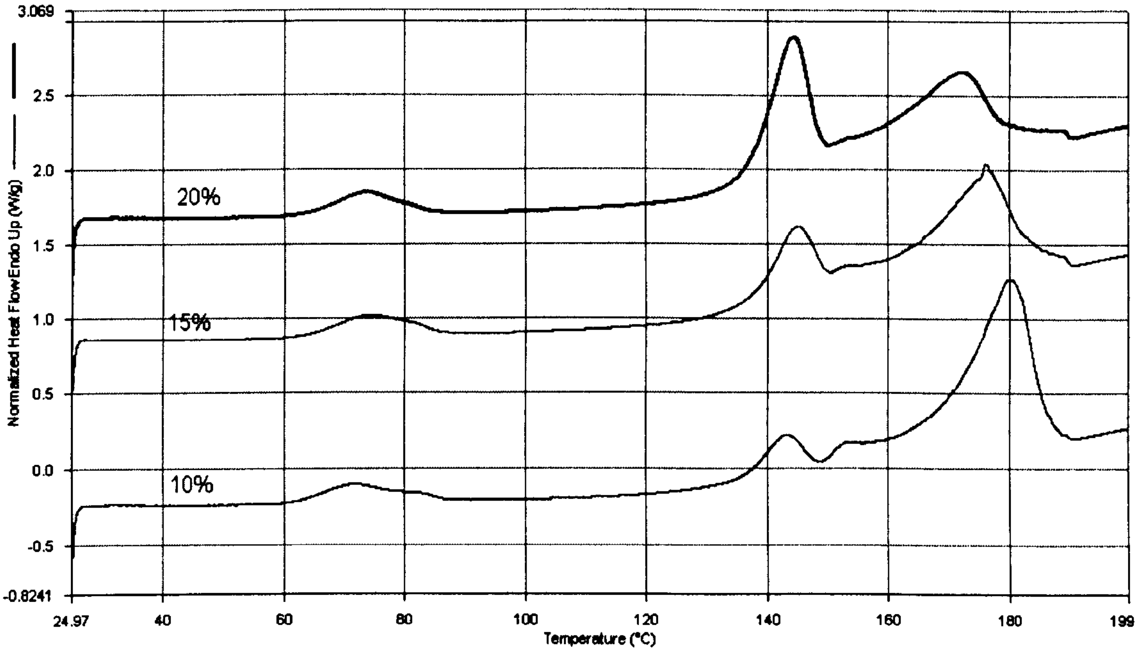


Figure 6.4: DSC traces obtained for the co-crystalline products prepared by the dry method with anhydrous glucose

Proportion of Anhydrous glucose added (%)	ΔH_{GM} (J/g)	ΔH_{AG} (J/g)	ΔH_S (J/g)	T_S (°C)
10	9.6	16.7	108.5	179.9
15	12.0	38.6	106.8	176.2
20	11.2	60.8	116.6	172.0

Table 6.1: DSC results obtained for the co-crystalline products prepared by the dry method with anhydrous glucose

In the case of the addition of glucose monohydrate to the co-crystallisation process at the proportions of 10 and 15%, no trace of crystalline glucose in the anhydrous form was observed and only the melting endotherm for glucose monohydrate and the two-peak pattern for sucrose appeared. As for the dry method, the temperature of the second peak of the melting endotherm of sucrose decreased with an increase in the level of glucose added.

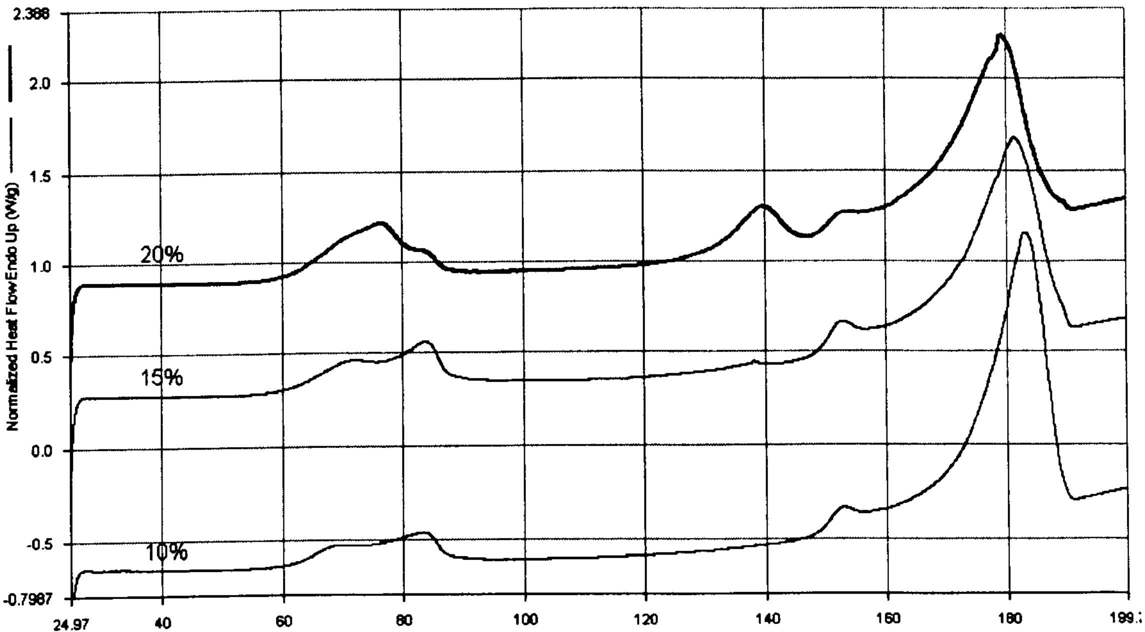


Figure 6.5: DSC traces obtained for the co-crystalline products prepared with glucose monohydrate

Proportion of glucose monohydrate added (%)	ΔH_{GM} (J/g)	ΔH_{AG} (J/g)	ΔH_S (J/g)	T_S (°C)
10	15.8	-	106.9	183.0
15	22.3	-	98.0	181.3
20	26.8	10.7	84.6	179.1

Table 6.2: DSC results obtained for the co-crystalline products prepared with glucose monohydrate

The results for the wet method showed no evidence for glucose in the anhydrous form whatever the proportion of glucose added. The high level of glucose found in its anhydrous form in the products obtained by the dry method can be explained by the fact that after the addition of the anhydrous glucose, not all the crystals were dissolved at the point at which sucrose crystallised. This induced the remaining glucose to crystallise in the anhydrous form preferentially.

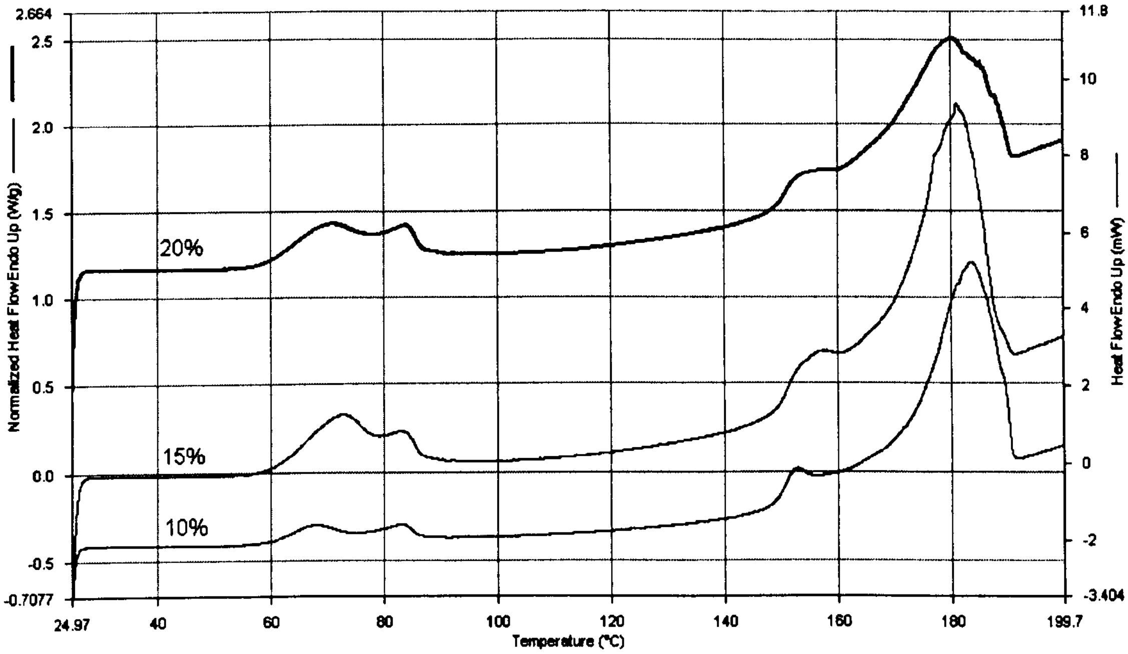


Figure 6.6: DSC traces obtained for the co-crystalline products prepared by the wet method

Proportion of glucose added (%)	ΔH_{GM} (J/g)	ΔH_S (J/g)	T_S (°C)
10	9.2	88.9	183.5
15	20.0	100.9	180.9
20	25.0	92.9	179.8

Table 6.3: DSC results obtained for the co-crystalline products prepared by the wet method

The co-crystallisation of sucrose with glucose has been studied recently by Bhandari *et al.*.[5] Their results showed no crystallisation of glucose in such mixtures apart for glucose monohydrate crystallising out after one month of storage. This disagreement in results is due to the different ways of producing the co-crystalline materials. Indeed, in their work, once glucose was added to the sucrose solution, the mixture was heated again to reach a temperature of 131°C, which was not the case in our study. Instead, we undertook to let the temperature drop after the addition of glucose and homogenisation.

Proportion of glucose (%)	Anhydrous glucose (Dry method)	Anhydrous glucose (Wet method)	Glucose monohydrate
10	1.1	0.9	0.9
15	1.7	1.3	1.2
20	1.8	1.6	1.2

Table 6.4: Moisture contents of the co-crystalline materials

The moisture contents of the materials obtained are shown in Table 6.4. For each of the three methods by which glucose was added to form the co-crystalline materials the moisture content increased with an increasing level of glucose added. This result is in accordance with the DSC data obtained which showed an increase in the amount of glucose in the monohydrate form with an increase in the proportion of glucose added. Nevertheless, the amount of water present cannot be explained solely by the amount of glucose monohydrate in the products. Indeed, though most of the glucose had crystallised in the anhydrous form, the dry method gave the higher values of moisture content for a similar proportion. In this case, contrary to the other products obtained the moisture is in a free form (i.e. not tightly bound) for the most part.

6.2.2. Effect of the temperature of re-crystallisation

The limits of temperature of re-crystallisation for the co-crystallisation process of the sucrose-glucose system were investigated. Sucrose (Fisher Chemicals) and anhydrous glucose in the proportion (85/15) were co-crystallised using the previous method (Method 9.3.1.1) but with varying temperatures of boiling to achieve different concentrations of the sucrose solution. It was found that decreasing the temperature of boiling of the sucrose solution increased the amount of water present in the mixture. Below 122°C, the product obtained was very soft and required a longer drying time. Above 133°C, the solution of sucrose began to show some signs of inversion (yellowish colour).

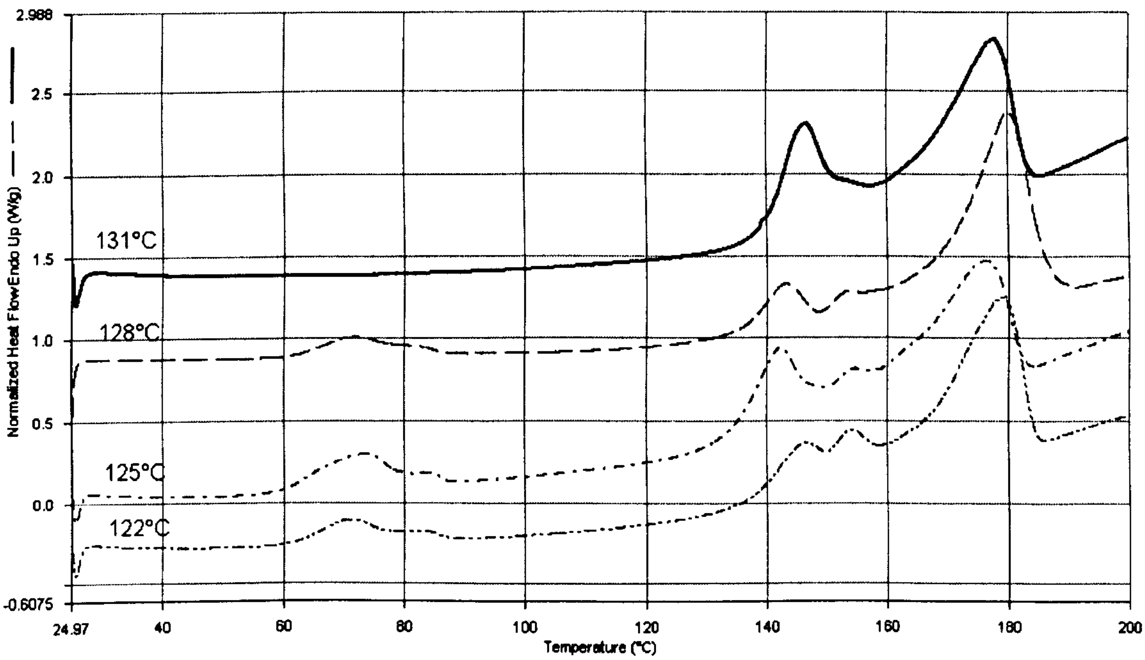


Figure 6.7: DSC traces obtained for the co-crystalline products prepared by the dry method with 15% of glucose added

Temperature of boiling (°C)	T_{GM} (°C)	ΔH_{GM} (J/g)	T_{AG} (°C)	ΔH_{AG} (J/g)	T_S (°C)	ΔH_S (J/g)
122	71.2	11.7	146.7	24.4	179.0	65.0
125	71.7	12.5	146.8	36.2	176.8	53.5
128	71.4	12.1	146.3	38.6	176.2	106.8
131	_	_	146.6	54.9	177.7	58.2

Table 6.5: DSC results obtained for the co-crystalline products prepared by the dry method with 15% of glucose added

As expected, it was found that from 122 to 131°C, at higher temperatures, re-crystallisation of glucose in the anhydrous form was favoured due to the lower amount of water present (Figure 6.7). When the sucrose solution was boiled to 131°C, no trace of glucose in the monohydrate form was detected on the DSC trace.

In view of seeking a potential use of the co-crystalline materials in the confectionery industry, the presence of glucose monohydrate in the co-crystalline product could be either advantageous or disadvantageous depending on the application. For instance, in the preparation of chocolate, the water of hydration could be released during the conching step.[6] Thus, in chocolate, the presence of water would be acceptable only if the moisture was bound tightly enough not to be released during chocolate manufacture. In contrast, for tabletting, glucose monohydrate has better compressibility properties than anhydrous glucose; hence its presence would be beneficial for the final hardness of the tablets.[7]

6.2.3. Effect of the commercial source of sucrose

The differences in crystallisation behaviour of the component sugars was found to be depending on the type of glucose added. Sucrose is not readily available in a hydrate form but some minor differences in purity due to different sources of the material have been found. It was thus intended to investigate the influence of the various sources of sucrose on the co-crystallisation of sucrose and glucose. Sucrose from Fisher Chemicals (an analytical grade reagent), Tate & Lyle and Silver Spoon (for normal domestic usage) was investigated. A more detailed discussion of the properties of the sugars from different sources is given in Chapter 7. These sugars were co-crystallised with anhydrous glucose in the proportion 80/20 by boiling a sucrose solution at 128°C. Once the material was at room temperature, it was filtered by centrifugal filtration. The experiments were done in duplicate. The DSC traces of the different co-crystalline materials were found to be quite similar (Figure 6.8). Each time, glucose re-crystallised as a mixture of the anhydrous and the monohydrate forms. The only difference is that when Silver Spoon sucrose was used, the DSC traces did not show the first melting peak for sucrose at 150°C.

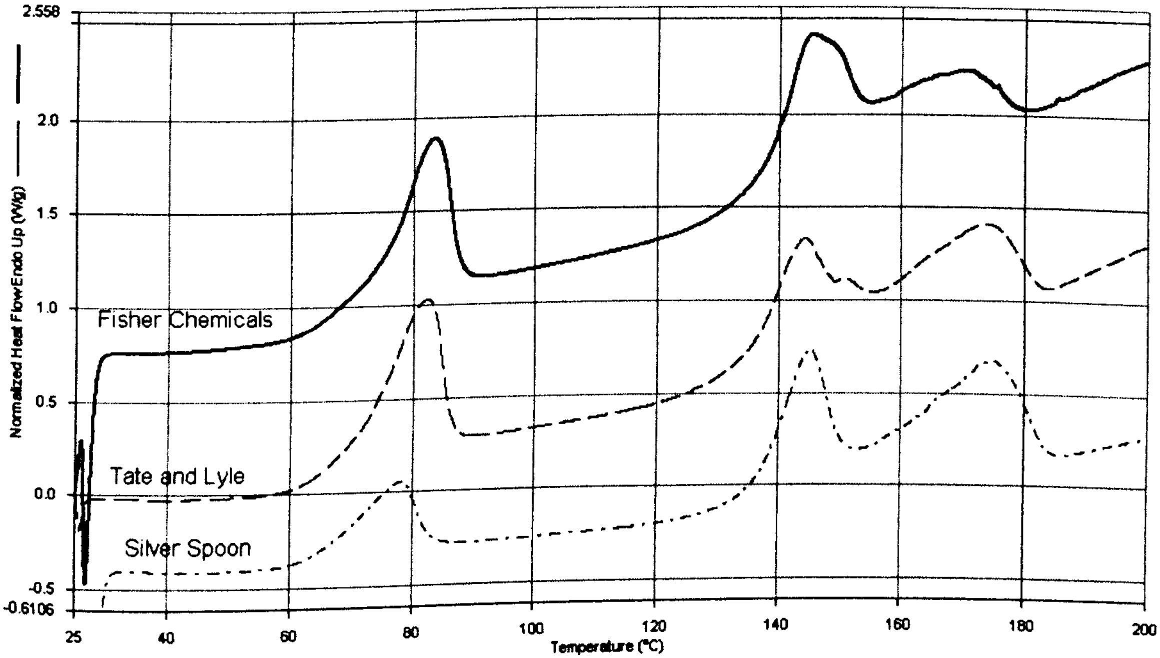


Figure 6.8: DSC traces obtained for the co-crystalline products prepared by the dry method with 20% of glucose added

Type of sucrose	T_{GM}(°C)	ΔH_{GM}(J/g)	T_{AG}(°C)	ΔH_{AG}(J/g)	T_S(°C)	ΔH_S(J/g)
FC	83.3 (± 0.1)	21.0 (± 1.1)	145.2 (± 0.7)	90.5 (± 2.5)	170.3 (± 0.4)	15.9 (± 0.6)
T&L	82.2 (± 0.3)	52.2 (± 2.0)	144.4 (± 0.3)	63.6 (± 1.9)	173.6 (± 0.1)	30.9 (± 0.8)
SP	77.6 (± 0.2)	27.3 (± 1.4)	143.7 (± 1.2)	60.2 (± 3.0)	175.3 (± 0.3)	48.1 (± 0.2)

Table 6.6: DSC results obtained for the co-crystalline products prepared by the dry method with 20% of glucose added

The proportion of filtrate obtained after centrifugal filtration for each source of sucrose is shown in Table 6.7. Consistently, the products prepared with Silver Spoon sucrose gave the lower amount of filtrate obtained after centrifugation and the sucrose from Tate & Lyle gave the highest amount of the three sugars. This result is linked to the rate of crystallisation of sucrose and glucose during the co-crystallisation process. This difference between the various sources of sucrose could be explained by some impurities being present. This difference of behaviour of the sucrose depending on its origin will be detailed in the next Chapter.

Type of sucrose	Fisher Chemicals	Tate & Lyle	Silver Spoon
Percentage of filtrate	10.1 (± 0.7)	14.4 (±2.1)	3.5 (±0.9)

Table 6.7: Percentage of filtrate by weight obtained after centrifugal filtration with sucrose from different sources

6.2.4. Incorporation of a flowing agent

Magnesium stearate and stearic acid are known to improve the flow properties of a powder. During compression, it is usual to add these additives as lubricants.[8] Rather than add this agent to the end-product by dry blending; it was thought advantageous to incorporate it during the co-crystallisation process in order to have a powder directly compressible with only the flavouring agent to be added. The flowability and the thermal behaviour of co-crystalline products in which a flowing agent (stearic acid or magnesium stearate) was incorporated during the co-crystallisation process (Method 9.3.1.2) were studied. The DSC traces and data of the products prepared are shown in Figures 6.9, 6.10 and Tables 6.8, 6.9 respectively for stearic acid and magnesium stearate.

When stearic acid was added in the co-crystalline material, its presence was observed on the DSC traces by a peak at 55°C. Furthermore, it was found to decrease the amount of glucose in the anhydrous crystalline form shown by the reduced intensity of the peak around 140°C.

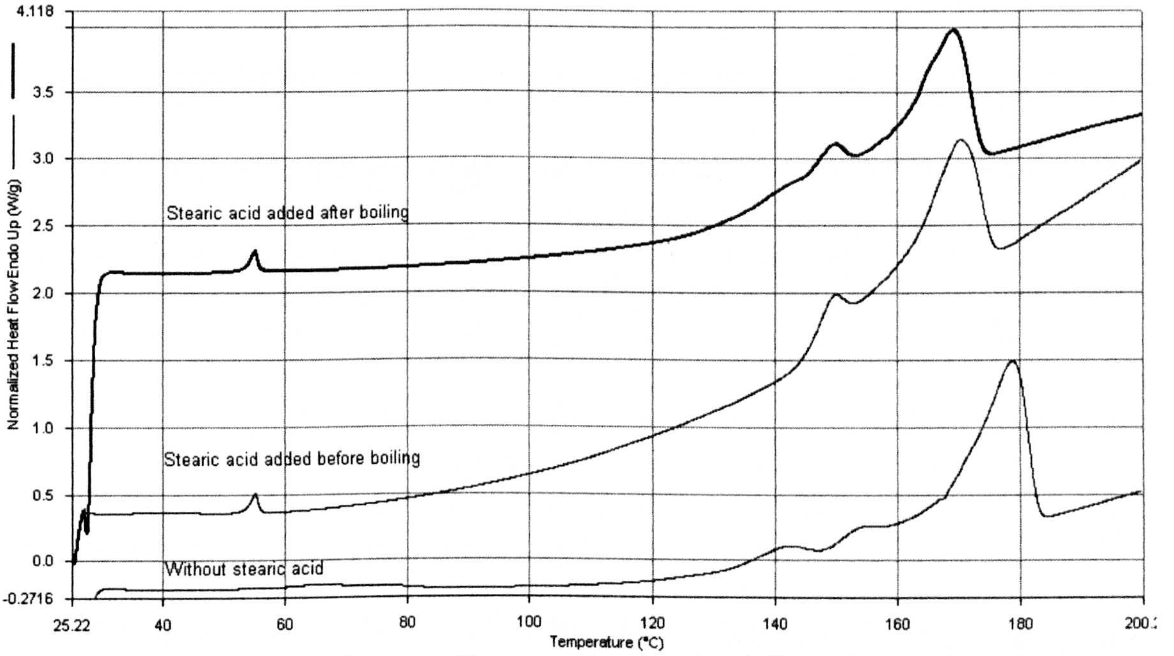


Figure 6.9: DSC traces of co-crystalline materials containing 10% of glucose and stearic acid

Material	T(°C)	ΔH(J/g)	T_{AG}(°C)	ΔH_{AG}(J/g)	T_{S}(°C)	ΔH_{S}(J/g)
Stearic acid added after boiling	55.0	1.7	–	–	169.2	84.0
Stearic acid added before boiling	55.0	14.7	–	–	170.3	81.6
Without stearic acid	–	–	141.6	3.8	178.8	74.4

Table 6.8: DSC results of co-crystalline materials containing 10% of glucose and stearic acid

When magnesium stearate was added in the co-crystalline material, its presence was not observed on the DSC traces in the range of temperatures studied (up to 200°C). Nevertheless, it increased the amount of crystalline glucose either in the monohydrate or the anhydrous form depending on the time of addition. Thus, when magnesium stearate was added to the initial sucrose solution, its presence delayed the crystallisation of glucose making it crystallise mainly when the temperature of the mixture was below 50°C. In contrast, when it was added at the same time as glucose, it induced crystallisation of the mixture giving a higher proportion of glucose in the anhydrous form.

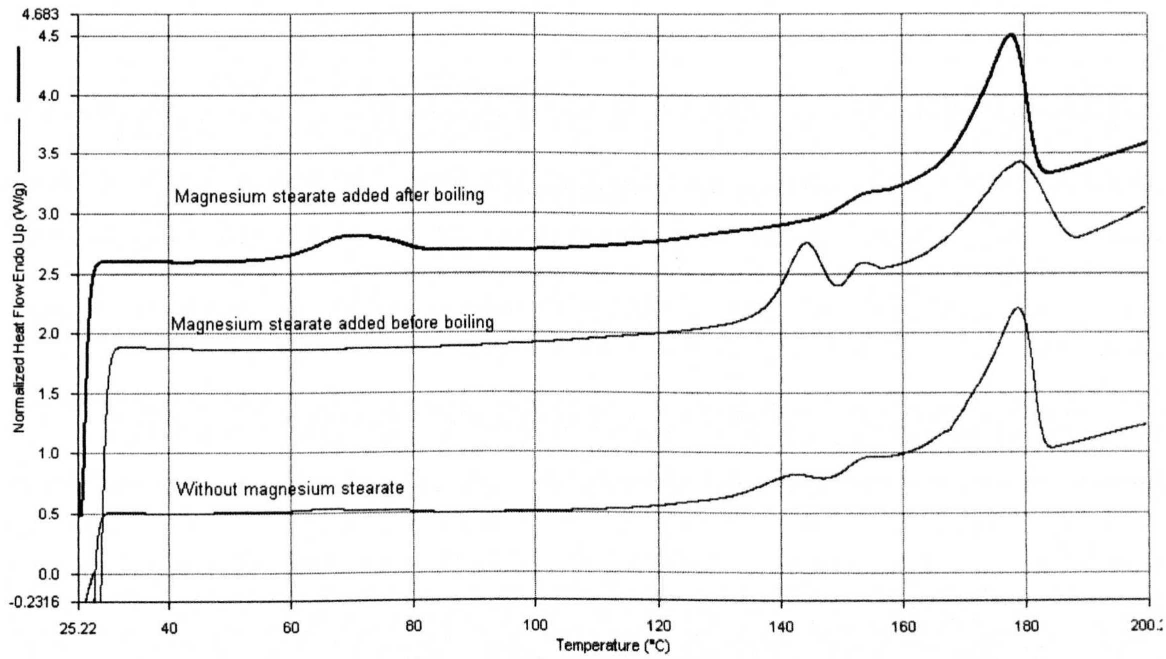


Figure 6.10: DSC traces of co-crystalline materials containing 10% of glucose and magnesium stearate

Material	T_{GM}(°C)	ΔH_{GM}(J/g)	T_{AG}(°C)	ΔH_{AG}(J/g)	T_S(°C)	ΔH_S(J/g)
Magnesium stearate added after boiling	69.7	14.7	–	–	177.8	79.6
Magnesium stearate added before boiling	–	–	144.1	16.9	179.3	61.3
Without magnesium stearate	–	–	141.6	3.8	178.8	74.4

Table 6.9: DSC results of co-crystalline materials containing 10% of glucose and magnesium stearate

The flowability of the materials was studied by measuring their angle of repose. The values were compared to those obtained with similar co-crystalline materials without flowing agent as well as a dry blend of the co-crystalline product and magnesium stearate (Table 6.10).

Product	Angle of repose (°)	Standard deviation
Without flowing agent	40.5	1.0
Acid stearic added before boiling	37.5	0.5
Acid stearic added after boiling	38.0	0.5
Magnesium stearate added before boiling	39.0	0.5
Magnesium stearate added after boiling	37.5	0.5
Dry mixture Co-cryst./mag. stearate	37.5	0.5

Table 6.10: Angle of repose of the powders

As expected, the angle of repose was lower for the dry mixture of the co-crystalline material and magnesium stearate than for the co-crystalline material alone. The flowability of all the materials in which the flowing agent had been incorporated during the co-crystallisation process had improved compared to those without the flowing agent. The lowest value was obtained when stearic acid was used and added at the same time as glucose.

6.3. Co-crystallisation sucrose-glucose: glucose as the main ingredient

In the literature, co-crystallisation materials most often involve sucrose as the main ingredient.[9] Nevertheless, some applications in the food industry could be advantaged by different proportions of sucrose and glucose. It was thus intended to produce co-crystalline materials with a majority of glucose. Starting from a sucrose solution, it was found difficult to increase the amount of glucose present in the co-crystalline material further than 20%, the mixture being very difficult to homogenise at this proportion. To obtain co-crystalline materials with a majority of glucose, the process has to start from a solution of glucose. Glucose solutions have higher boiling temperatures at atmospheric pressure than those of sucrose. In addition, glucose is more soluble than sucrose above 50°C. As a consequence, the co-crystallisation process cannot be directly applied to glucose. Indeed a boiling sucrose solution above 80% concentration (w/w) is saturated and prone to crystallise when only a slight drop in temperature is applied.[10] Thus, due to the differences between glucose and sucrose in relation to solubility in aqueous systems and Boiling Point Elevation values,[11] preparation of saturated solutions of each of the sugars requires different protocols. For example, when a boiling glucose solution is used in order to prepare a supersaturated solution, it needs either to be cooled by several degrees[12] or to have been concentrated under vacuum[13] to achieve a lower point of ebullition. These two methods have been investigated for the preparation of co-crystalline materials containing a majority of glucose.

6.3.1. Experiments under vacuum

The process used (Method 9.3.1.3.1) was based on that described in the patent US 4,342,603 by M.J. Daniels[13]. The experiments were made in duplicate, with the second series involving a longer time of concentration under vacuum. After the co-crystallisation process, the products were filtered under centrifugation to remove any mother liquor.

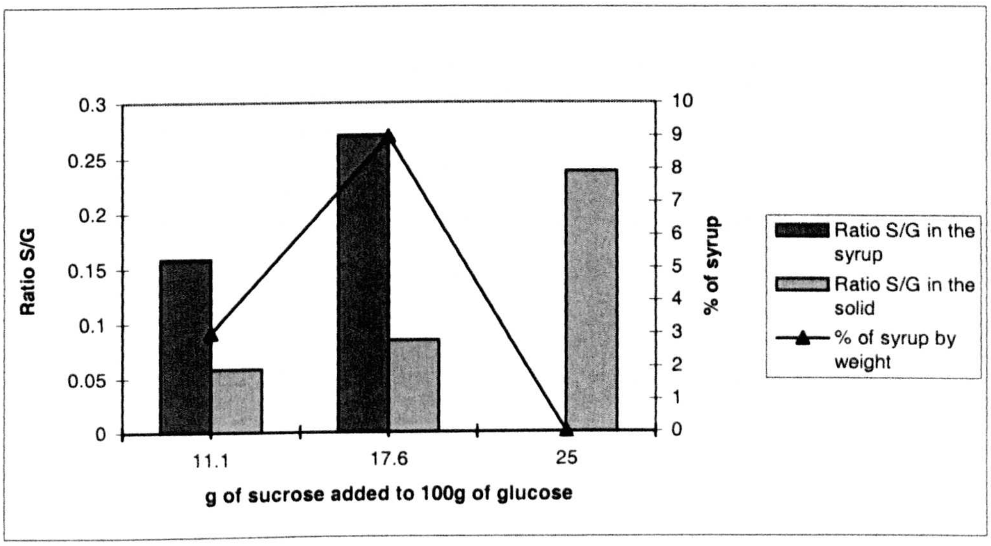


Figure 6.11: Proportion of sucrose in the crystals and the filtrate after centrifugation

Then, both the crystals and the filtrate were analysed by HPLC. With the second series of experiments no syrup was obtained. Figure 6.11 shows the amount of syrup obtained after centrifugation as well as the ratio of sucrose/glucose in the crystals and in the filtrate. The variation of the amount of filtrate obtained can be explained by the lack of reproducibility of the concentration of the solution. A large amount of second ingredient namely sucrose was found in the filtrate after centrifugation but it was found to a much less extent than with the reverse proportions (i.e. when glucose was the second ingredient). It can be concluded that increasing the amount of sucrose in the co-crystalline process resulted in an increase in the level of sucrose present in the filtrate.

Each product was examined by DSC from 25°C at 10°C/min (Figure 6.12). The traces of the samples containing only glucose (i.e. materials for which glucose was put through the co-crystallisation process as a blank) showed that glucose had crystallised almost completely in the monohydrate form for the first series. On the contrary, the second attempt showed only a small proportion of about 15% of glucose monohydrate (Figure 6.13) indicating that a larger amount of water had been removed by increasing the time of evaporation.

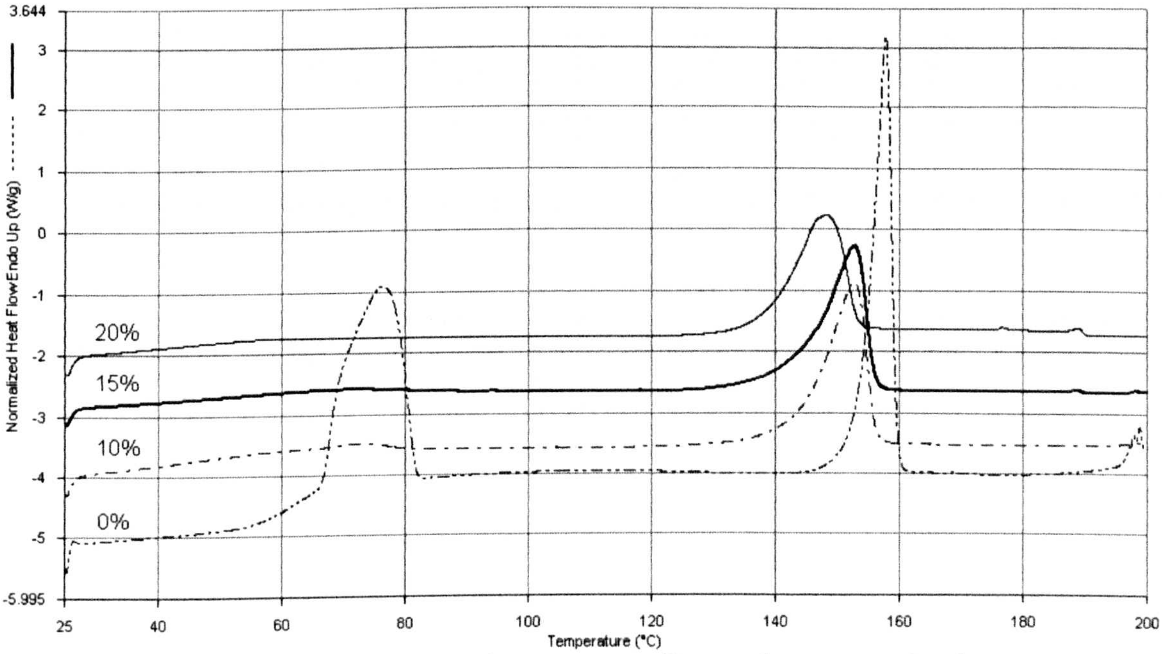


Figure 6.12: DSC traces of sucrose-glucose co-crystalline products prepared under vacuum

Amount of sucrose (%)	T_{GM}(°C)	ΔH_{GM}(J/G)	T_{AG}(°C)	ΔH_{AG}(J/G)
0	76.2	231.2	157.8	168.4
10	–	–	152.7	133.9
15	–	–	152.8	128.4
20	–	–	148.3	113.3

Table 6.11: DSC results of sucrose-glucose co-crystalline products prepared under vacuum

The DSC traces of co-crystalline products containing sucrose showed a glass transition around 40°C indicative of the presence of amorphous matter, such was observed even after centrifugation, and a peak at about 150°C which represents the fusion of anhydrous α-D-glucose. In one case (second series, 20% of sucrose) this peak was broader (Figure 6.13) which might be due to the presence of anhydrous β-D-glucose. This hypothesis was reinforced by optical rotation measurements undertaken on freshly prepared solutions of the materials. The results showed a percentage of about 15% of anhydrous β-D-glucose present in the co-crystalline material containing 20% of sucrose. No peak showing the fusion of crystalline sucrose was observed. The products usually decomposed around 185°C. As might be expected, an increase in the amount of sucrose decreased the temperature of melting of the crystalline anhydrous glucose. Only one sample among the series was analysed by XRD but it showed traces of sucrose in the crystalline form that was not visible by DSC.

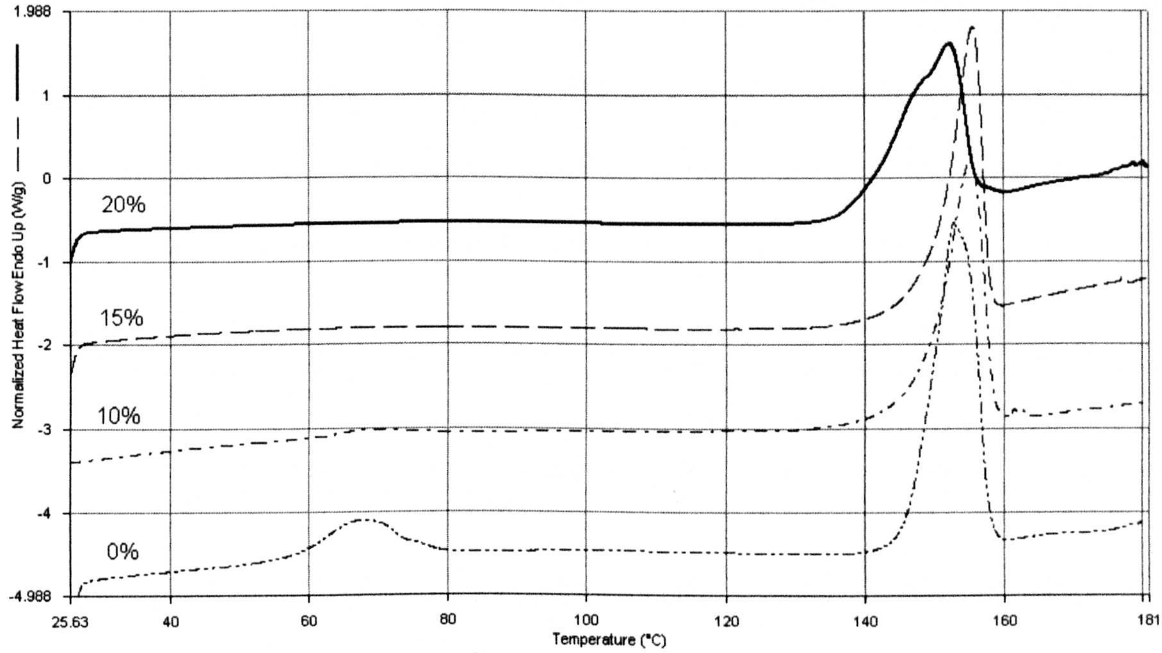


Figure 6.13: DSC traces of co-crystalline products prepared under vacuum at a higher level of supersaturation

Amount of sucrose (%)	T_{GM}(°C)	ΔH_{GM}(J/G)	T_{AG}(°C)	ΔH_{AG}(J/G)
0	67.5	34.7	152.9	167.4
10	–	–	155.2	130.4
15	–	–	153.0	117.1
20	–	–	152.2	121.6

Table 6.12: DSC results of co-crystalline products prepared under vacuum at a higher level of supersaturation

6.3.2. Experiments at atmospheric pressure

Initial experiments were carried out with a starting glucose solution containing 99 g of glucose for 70 mL of water. It was observed that when this solution was heated from 128 to 137°C a yellowish coloration appeared resulting from a partial decomposition of the sugar. The initial concentration of glucose was increased to 99 g of glucose for 30 mL of water in order to diminish the heating time and thus limit decomposition reactions. Once the co-crystallisation process was applied, the mixture was filtered under centrifugation. In each case, no syrup was obtained after filtration. The consistency of the products obtained is shown in Table 6.13. By increasing the temperature of re-crystallisation and the amount of sucrose, the mixture obtained passed from being brittle to being a sticky paste. The paste was not further investigated due to its not being of use in a commercial application. After centrifugation, the products were dried in a desiccator over P_2O_5 overnight and then ground to a fine powder.

Boiling temperature (°C)	Percentage of sucrose		
	10	15	20
115	Brittle	Brittle	Sticky paste
118	Brittle	Sticky paste	–
123	Brittle	Sticky paste	–

Table 6.13: Consistency of the co-crystalline products prepared by concentration at atmospheric pressure

As expected the moisture content of the co-crystalline products prepared at atmospheric pressure decreased when the temperature at which the solution had been boiled increased (Table 6.14). Overall, the figures obtained are smaller than those obtained with the experiments under vacuum, which were around 4%. It is believed that the water remaining is not tightly bound and can be removed by further drying.

Boiling temperature (°C)	Percentage of sucrose	
	10	15
115	3.0	2.6
118	2.3	–
123	2.2	–

Table 6.14: Percentage of water contained in the co-crystalline products obtained by concentration at atmospheric pressure.

The DSC trace of the sample containing only glucose showed that it has crystallised almost completely in the anhydrous form (Figure 6.14). The DSC traces of the products containing 10 and 15% of sucrose were similar to those obtained by concentrating under vacuum (Figure 6.15), that is to say that they showed a glass transition, a peak of fusion of anhydrous glucose, no trace of crystalline sucrose and an early decomposition at 185°C. It was found that an increase in the amount of sucrose decreased the temperature of melting of anhydrous glucose and gave a broader peak (Figure 6.14). The same results were obtained by increasing the temperature of the solution used for re-crystallisation (Figure 6.15).

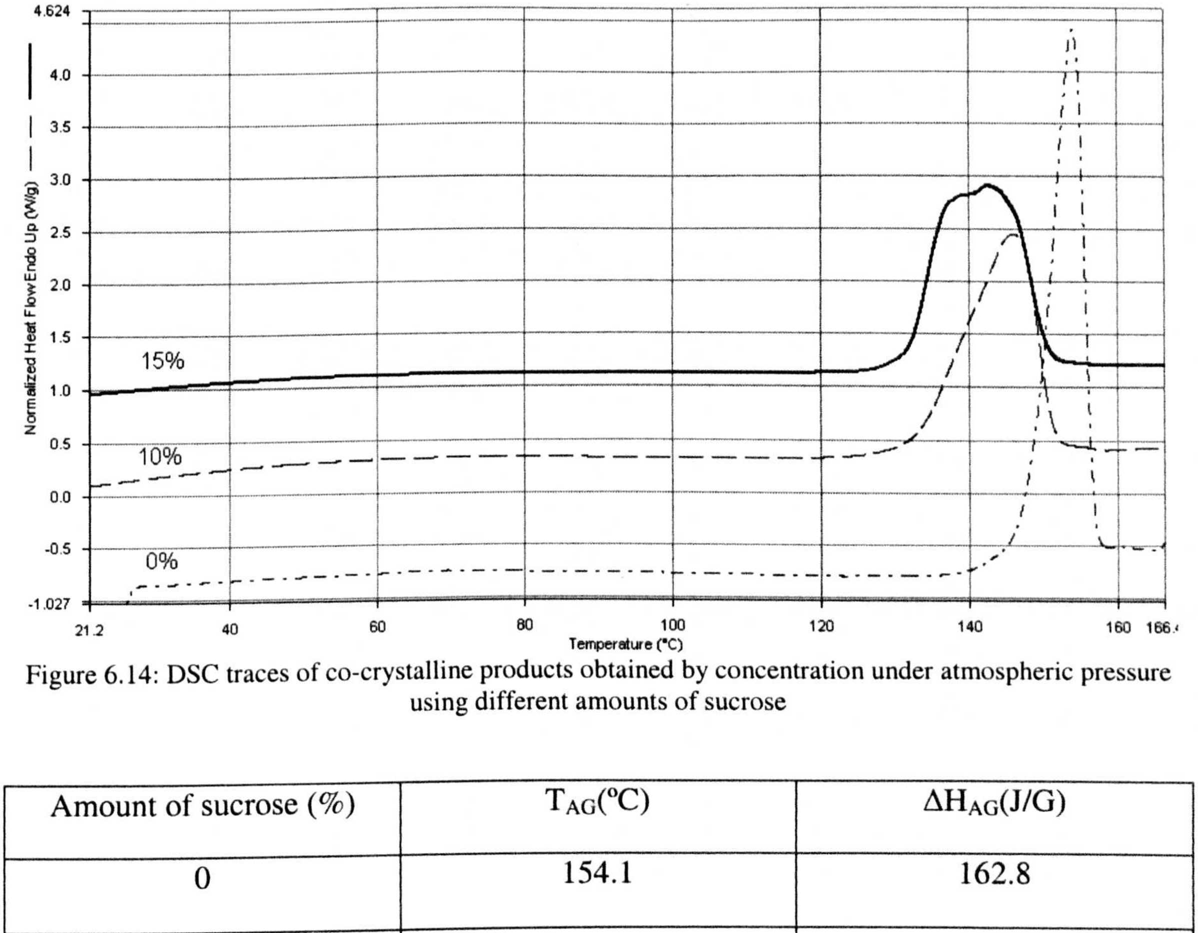


Figure 6.14: DSC traces of co-crystalline products obtained by concentration under atmospheric pressure using different amounts of sucrose

Amount of sucrose (%)	T_{AG}(°C)	ΔH_{AG}(J/G)
0	154.1	162.8
10	146.1	138.7
15	142.5	145.9

Table 6.15: DSC results of co-crystalline products obtained by concentration under atmospheric pressure using different amounts of sucrose

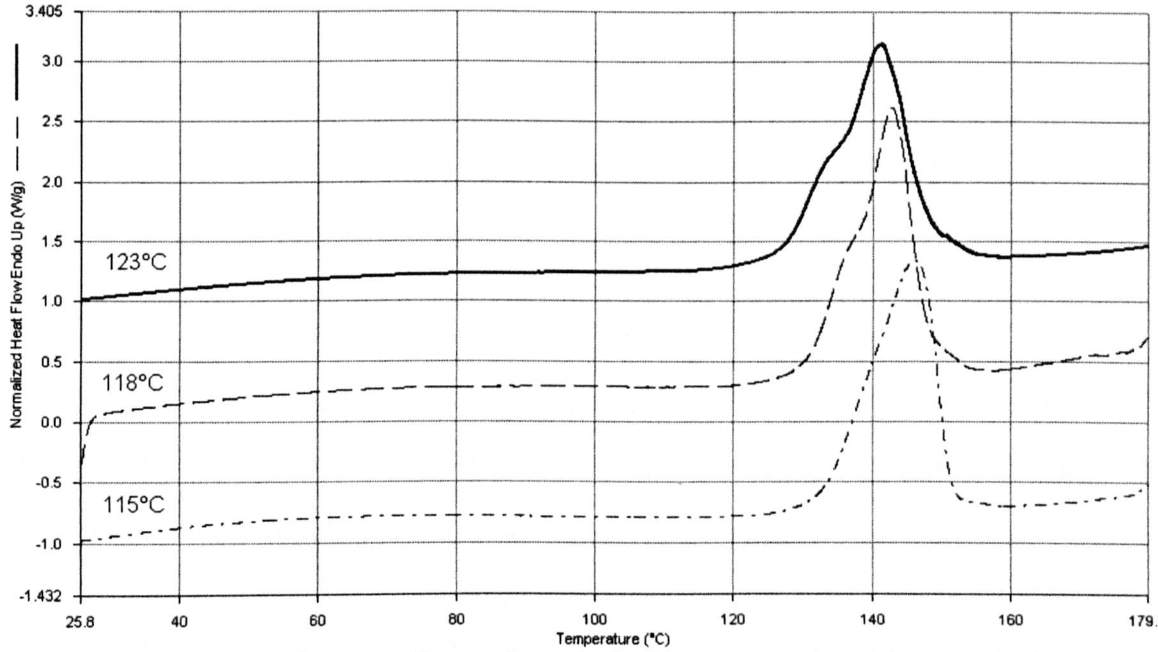


Figure 6.15: DSC traces of co-crystalline products obtained by concentration under atmospheric pressure using different temperatures of re-crystallisation

Temperature of re-crystallisation (°C)	T_{AG}(°C)	ΔH_{AG}(J/G)
115	146.1	138.7
118	142.9	134.2
123	141.2	136.2

Table 6.16: DSC results of co-crystalline products obtained by concentration under atmospheric pressure using different temperatures of re-crystallisation

The apparatus used for the concentration of the glucose solution under vacuum lacked accurate control of temperature and pressure; hence the resulting solutions of glucose were inconsistent in their final water contents.

At atmospheric pressure, there was a significant risk of decomposition reactions occurring during the concentration of the glucose solution. At high boiling temperatures and high sucrose content, the consistency of the products made them difficult to handle. In both methods, the use of seeds was required to nucleate the solutions. All of the sucrose dissolved during the process and remained mainly in an amorphous form though traces of sucrose were found by powder X-ray analysis. Furthermore, it was found that a more concentrated glucose solution and a higher amount of sucrose increased the final proportion of β-D-glucose in the product.

6.3.3. Experiments with molten glucose monohydrate

The previous methods used to prepare the co-crystalline products containing a majority of glucose have afforded poorly reproducible results. In addition, they have required the use of centrifugal filtration and, in some cases amorphous matter was present. Therefore, another way of preparing the co-crystalline materials was sought. Thus it was envisaged that starting from molten glucose would permit the materials to co-crystallise at relatively low temperatures and possibly enable a low initial moisture content to be achieved. Thus experiments were conducted using three different temperatures of re-crystallisation 110, 120 and 130°C and three different amounts of sucrose. The impact on the moisture content, water activity, flowability, melting endotherm and crystalline state of the products was studied.

During the co-crystallisation process, it was noticed that when 5% of sucrose was co-crystallised with glucose, the crystallisation took longer than when glucose was re-crystallised by itself. Furthermore, the products containing 15% of sucrose were stickier than those possessing 10% before they were dried. Increasing the percentage of sucrose to 20% gave a sticky paste which took too long to crystallise to be suitable for applications.

The results obtained for the moisture content of the products prepared are shown in Table 6.18. As a general trend, the moisture content increased with increasing levels of sucrose and slightly with higher temperatures of re-crystallisation. The increase in moisture content with temperature was not expected since a larger amount of water was removed by further heating. This result could be explained by the mixtures being more hygroscopic. The determination of water content is not sufficiently informative in relation to the influence of water on the physical properties of food.[14] Instead, this influence is dependent on the state of the water present which is expressed as water activity.[15] The water activity accounts for the availability of water to enter in reactions. It can affect the shelf life, odour, colour and texture of food. The results obtained for the water activity measurements are shown in Table 6.17. The water activity also increased with increasing level of sucrose which means that this extra moisture is not closely bound to the material. As sugars are more hygroscopic in their amorphous state, it would indicate that the proportion of amorphous matter increased with the temperature and the amount of sucrose.

% of sucrose Temperature of re-crystallisation (°C)	0	5	10	15
110	0.336	0.281	0.457	0.668
120	0.331	0.560	0.669	0.654
130	0.341	0.396	0.664	0.659

Table 6.17: Water Activity of the co-crystalline sucrose-glucose products prepared from molten glucose monohydrate

% of sucrose Temperature of re-crystallisation (°C)	0	5	10	15
110	0.6	0.8	0.3	1.7
120	0.6	1.0	2.0	1.3
130	0.6	1.0	2.1	1.9

Table 6.18: Moisture Content of the co-crystalline sucrose-glucose products prepared from molten glucose monohydrate

All of the DSC traces of the products prepared are shown in Appendix 1. They all showed two peaks around 150 and 155°C assigned to α and β-anhydrous glucose respectively. Tables 6.19, 6.20, 6.21 give the DSC data for the co-crystalline materials prepared at different proportions of the component sugars and temperatures of the solutions used to form the co-crystalline materials.

Amount of sucrose (%)	Tα(°C)	ΔHα(J/g)	Tβ(°C)	ΔHβ(J/g)
0	150.9	154.0	154.9	14.6
5	147.5	134.7	151.3	15.4
10	150.3	135.3	153.1	34.4
15	142.1	129.3	147.9	21.2

Table 6.19: DSC results for the co-crystalline products re-crystallised at 110°C

Amount of sucrose (%)	Tα(°C)	ΔHα(J/g)	Tβ(°C)	ΔHβ(J/g)
0	150.0	129.5	155.0	37.2
5	146.7	109.0	152.1	38.8
10	142.3	98.7	150.6	52.0
15	141.5	132.6	147.8	21.4

Table 6.20: DSC results for the co-crystalline products re-crystallised at 120°C

Amount of sucrose (%)	Tα(°C)	ΔHα(J/g)	Tβ(°C)	ΔHβ(J/g)
0	150.5	121.6	155.4	41.3
5	144.6	73.8	152.2	65.7
10	141.4	87.1	150.6	56.8
15	140.7	112.9	148.3	33.6

Table 6.21: DSC results for the co-crystalline products re-crystallised at 130°C

Figure 6.16 shows the proportion of anhydrous α-D-glucose with varying the temperature and sucrose concentration. The values are approximate since the two peaks overlap each other. As expected, the percentage of α-glucose decreased when the temperature of re-crystallisation was increased. The addition of 5 and 10% of sucrose at the point of crystallisation decreased the proportion of α-glucose present in the co-crystalline products. In contrast, the trend was reversed when the mixture was charged with 15% of sucrose.

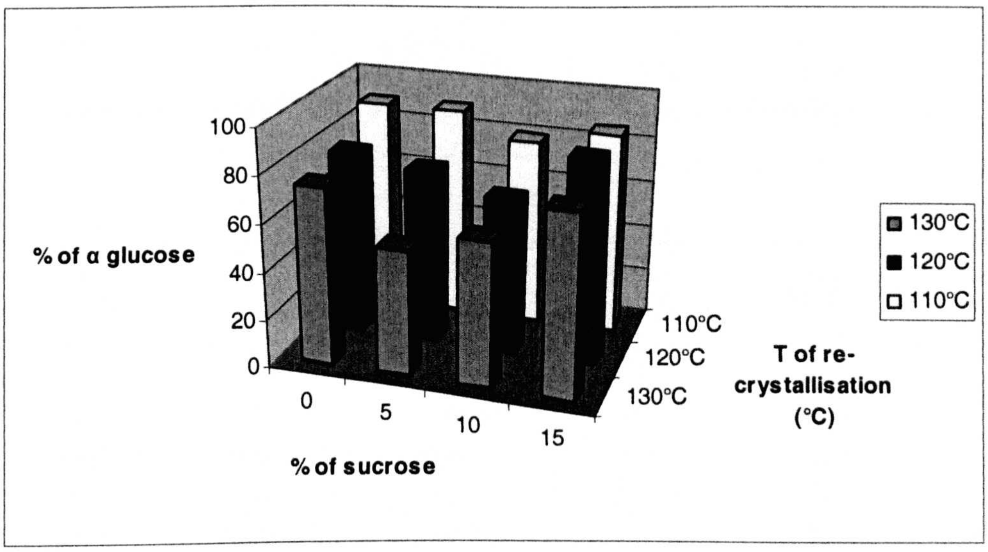
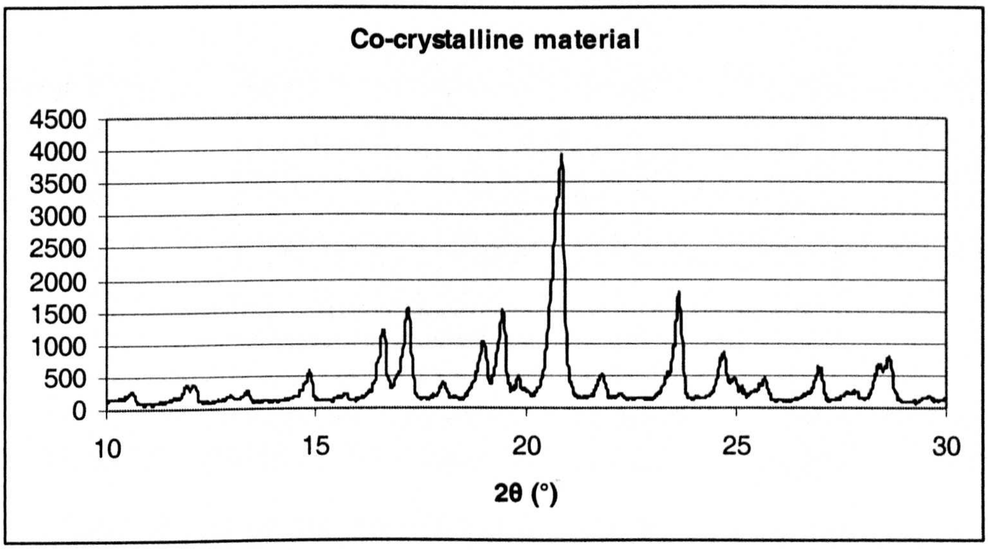
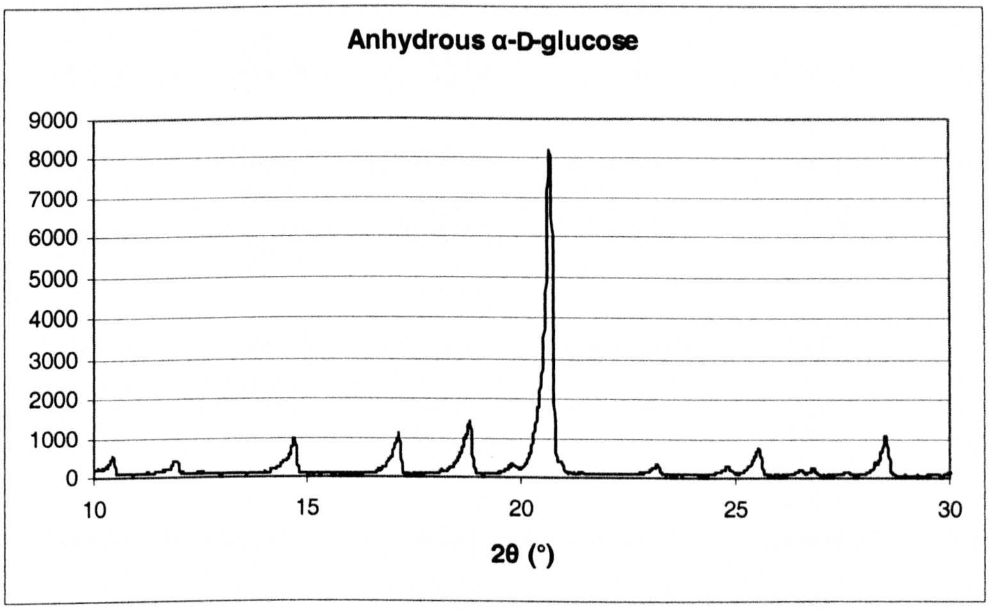


Figure 6.16: Proportion of α-anhydrous glucose present in the co-crystalline products

The X-ray diffraction analysis of the materials showed that sucrose was present in a crystalline state in all of the products obtained; sucrose could be observed by the appearance of two small peaks for a 2θ at 13° (Figure 6.17).





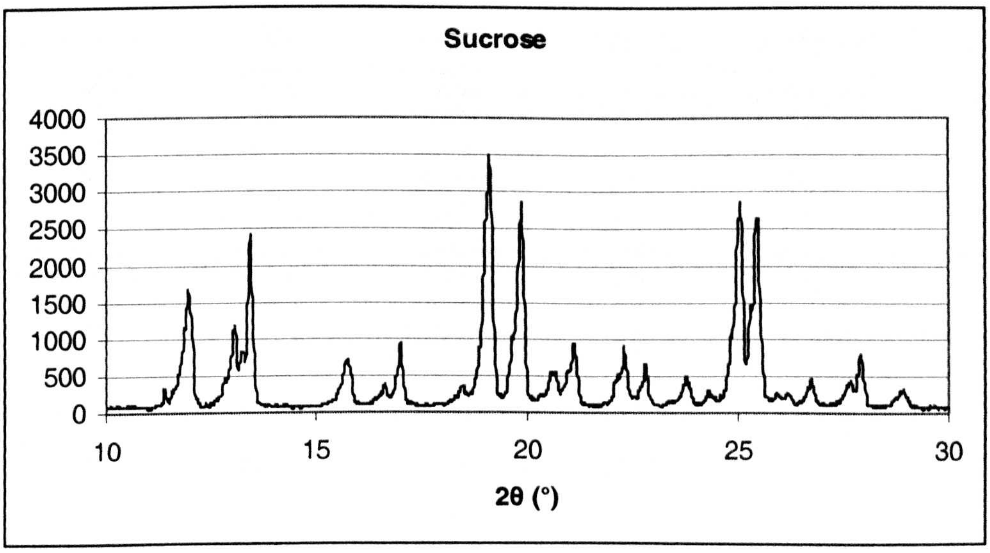


Figure 6.17: X-Ray diffraction patterns: co-crystalline material containing 10% of glucose; anhydrous α-D-glucose; sucrose

% of sucrose Temperature of re-crystallisation (°C)	0	5	10	15
110	35.0 (0.5)	32.5 (0.5)	36.5 (1.0)	37.5 (1.5)
120	35.5 (1.0)	33.0 (1.0)	37.5 (1.5)	39.0 (1.0)
130	33.0 (1.0)	34.0 (0.5)	34.5 (0.5)	38.5 (0.5)

Table 6.22: Angle of repose of the co-crystalline sucrose-glucose products prepared from molten glucose monohydrate. The standard deviation is in brackets.

The increase in temperature of re-crystallisation did not significantly influence the flowability of the powder on the basis of angle of repose measurements. However, an increase in the amount of sucrose present in the mixtures gave a slightly less free-flowing powder (Table 6.22). The increase in moisture content and water activity could be responsible for the increase in cohesiveness of the powder since the lumping of food powders is generally caused by the wetting of particle surface.[16]

6.3.4. Incorporation of a flowing agent

The flowability and thermal behaviour were studied of co-crystalline products to which a flowing agent (stearic acid or magnesium stearate) had been incorporated during the co-crystallisation process (Method 9.3.1.3.4). The DSC traces and data obtained for the products prepared are shown in Figures 6.18, 6.19 and Tables 6.23, 6.24 respectively for stearic acid and magnesium stearate additions.

When stearic acid was added to the co-crystalline materials, its presence was observed on the DSC traces by a peak at 55°C. The presence of stearic acid appeared to decrease the proportion of glucose present in the β form.

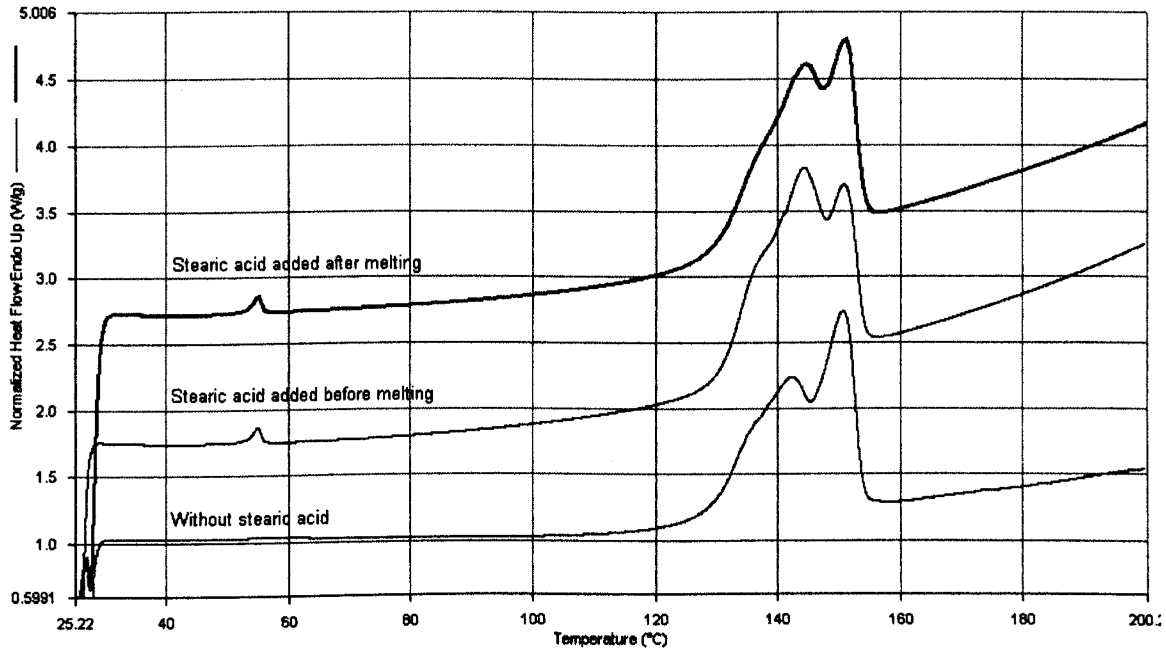


Figure 6.18: DSC traces of co-crystalline materials containing 90% of glucose and stearic acid

Material	T(°C)	ΔH(J/g)	Tα(°C)	ΔHα (J/g)	Tβ(°C)	ΔHβ (J/g)
Stearic acid added after melting	55.1	1.6	144.6	116.3	151.0	39.7
Stearic acid added before melting	55.0	1.4	144.3	131.1	150.8	32.2
Without stearic acid	_	_	142.2	67.5	149.7	73.5

Table 6.23: DSC results of co-crystalline materials containing 90% of glucose and stearic acid

In contrast, when magnesium stearate was used, its presence could not be detected on the DSC traces obtained (Figure 6.19). Nevertheless, when it was added after the melting of glucose monohydrate, it was found to increase significantly the proportion of anhydrous β-D-glucose.

The flowability of the materials was studied by measuring their angle of repose (Table 6.25). The values were compared to those obtained of similar co-crystalline materials without flowing agent as well as a dry blend of the co-crystalline product and magnesium stearate.

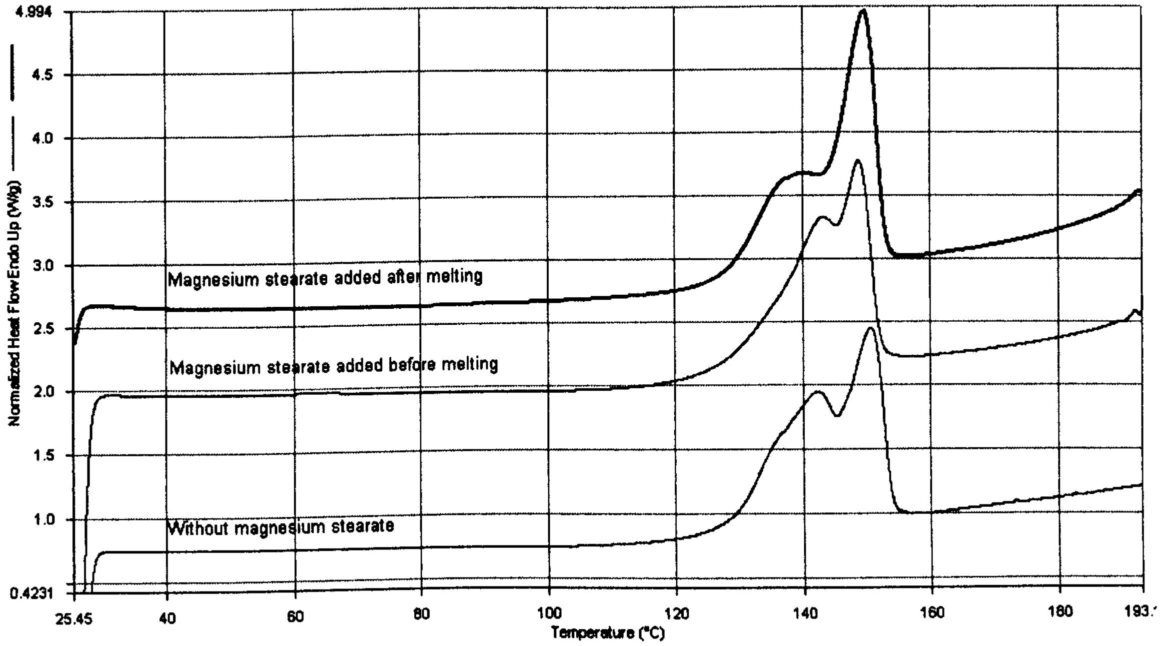


Figure 6.19: DSC traces of co-crystalline materials containing 90% of glucose and magnesium stearate

Material	Tα(°C)	ΔHα (J/g)	Tβ(°C)	ΔHβ (J/g)
Magnesium stearate added after melting	140.2	67.5	149.7	73.5
Magnesium stearate added before melting	143.3	90.9	148.8	45.4
Without magnesium stearate	142.3	84.4	150.6	52.2

Table 6.24: DSC results of co-crystalline materials containing 90% of glucose and magnesium stearate

As expected, the angle of repose was found to be lower for the dry mixture of co-crystalline material and magnesium stearate than for the co-crystalline material alone. The flowability of all the materials to which the flowing agent had been incorporated during the co-crystallisation process had improved compared to those without the flowing agent. The lowest value was obtained when magnesium stearate was used and was added at the same time as sucrose.

Product	Angle of repose (°)	Standard deviation
Without flowing agent	40.0	0.5
Acid stearic added before melting	37.5	0.5
Acid stearic added after melting	39.5	1.0
Magnesium stearate added before melting	38.5	0.5
Magnesium stearate added after melting	37.5	0.5
Dry blend co-cryst./mag. stearate	39.0	0.5

Table 6.25: Angle of repose of the co-crystalline products containing of flow agent

6.4. Phase diagrams obtained from dry blends

In the previous sections, the co-crystallisation of sucrose with glucose was performed by a method which involves the dissolution and re-crystallisation of the sugars in water. However, water can be considered as a third component of the system. To understand better the results obtained from the thermal analyses of the co-crystalline products, the construction of the sucrose-glucose phase diagram was undertaken using a method that did not involved the use of water. The possibility of the formation of a co-crystal by this method was also studied.

Mixtures of icing sugar and anhydrous α-D-glucose (Fisher Chemicals) were prepared using a mortar and a pestle. DSC and X-ray powder diffraction measurements were carried out on each sample. DSC measurements were taken by heating the sample from 25 to 200°C. The phase diagram, shown in Figure 6.20, was constructed using the peak values for melting and their onset on the DSC curves.

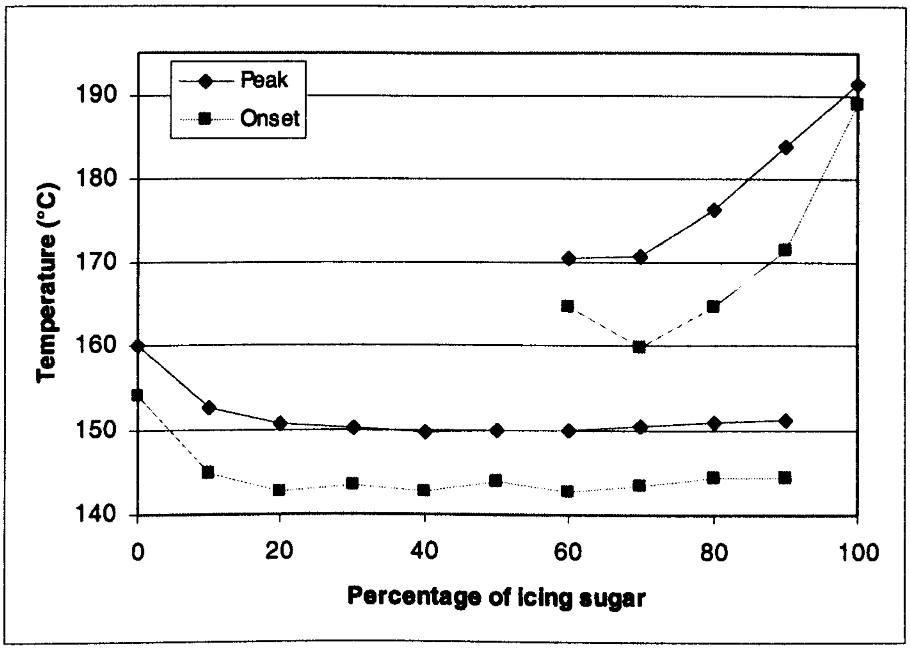


Figure 6.20: Phase diagram sucrose-glucose using icing sugar

The phase diagram for the system appeared to be eutectic though there was only one melting peak when the proportion of sucrose was below 50%. For each of the mixtures, X-ray powder diffraction ascertained that sucrose was still crystalline after the grinding.

The experiment was repeated using a mixture of granular sucrose and anhydrous α-D-glucose both from Fisher Chemicals. This time more fractions were prepared using two methods: grinding the reagents separately and then mixing them or grinding them together. The phase diagrams obtained when the products were ground separately and together are shown in Figures 6.21 and 6.22 respectively.

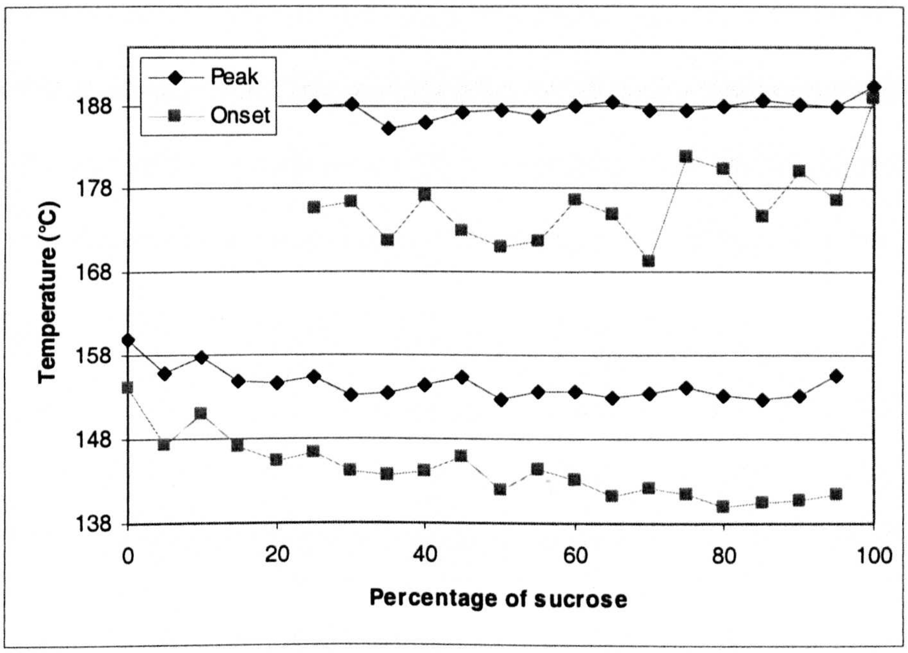


Figure 6.21: Phase diagram sucrose-glucose with the materials milled separately

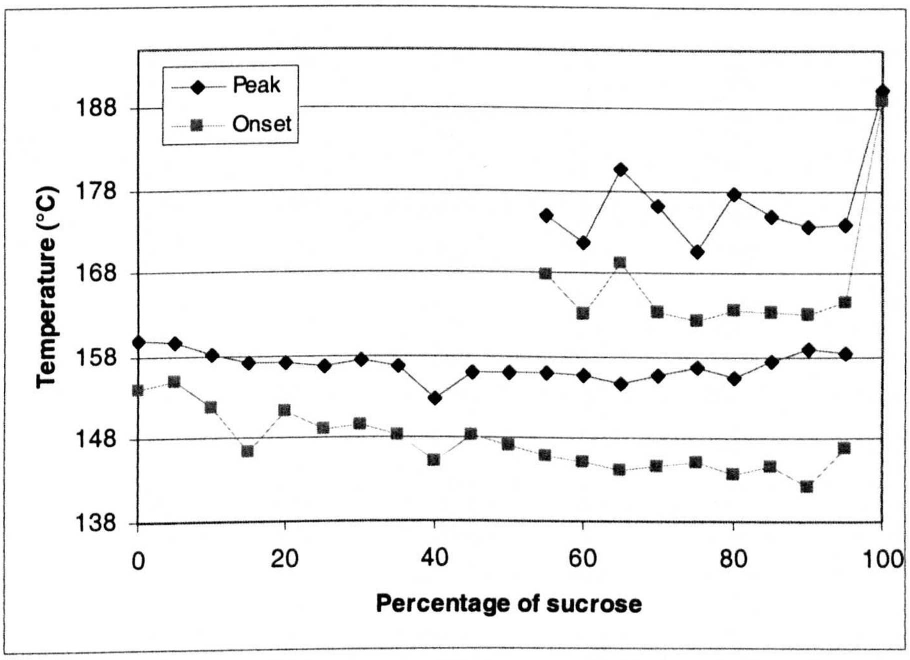


Figure 6.22: Phase diagram sucrose-glucose with the materials milled together

When the reagents were ground separately almost no change in the respective melting points was observed. The melting peak of sucrose only disappeared when it was present at a proportion below 20%. On the contrary, when the materials were ground together the melting point of the mixture decreased significantly as the proportion of glucose increased. On the other hand, the melting point of glucose remained almost the same whatever the proportions of both sugars. One hypothesis could be that the melting point of the eutectic formed by the sugars and the melting point of glucose are too close to be distinguished. Another is that at a high proportion of glucose, the products form a solid solution.

Figure 6.23 shows the sucrose-glucose phase diagram when the two materials were ground for a longer period together (2 min instead of 1).

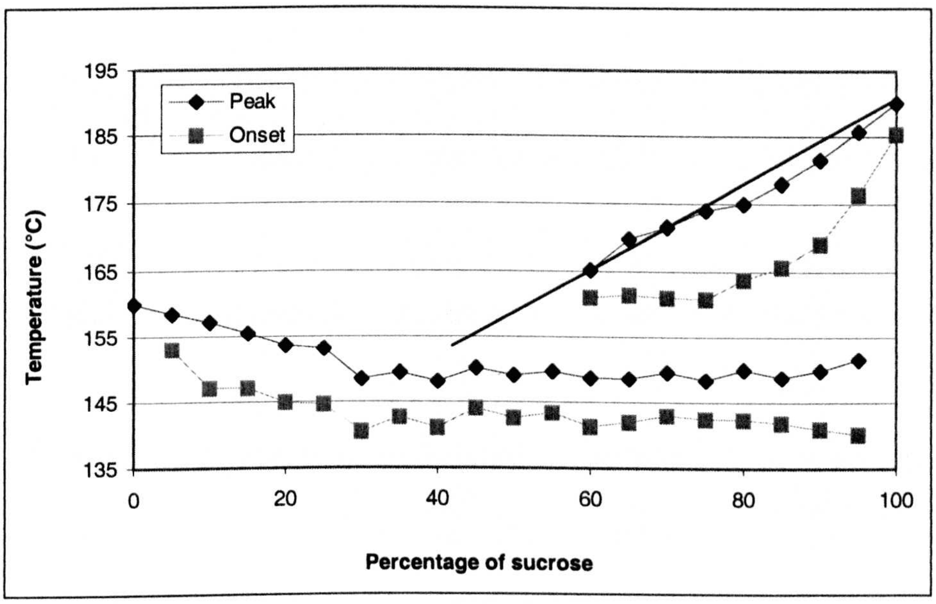


Figure 6.23: Phase diagram sucrose-glucose with the materials milled together for a longer time

Similar results from the previous diagrams were obtained i.e. above 40% of glucose present in the mixture only one melting point was observed but the curves obtained were smoother than those previously obtained (Figures 6.20 and 6.22). These results confirm that DSC analysis is not sufficient to determine whether sucrose is in a crystalline form or not when it is present in a minority with glucose. Thus, X-ray powder diffraction should be used as a complementary analysis. Furthermore, by calculating the trendline of the curve formed by the peaks of the melting points of sucrose, a theoretical intersection with the eutectic can be found at 33% of sucrose, which would be the possible proportion of the co-crystalline mixture. Nevertheless, X-ray analysis did not show any peaks other than those for sucrose and glucose pattern. Thus, the presence of a co-crystalline phase was not detected.

6.5. Conclusion

Co-crystallisation of sucrose and glucose has been first carried out in the proportions 0-20% of glucose. The type of glucose, commercial source of sucrose and the temperature of the supersaturated solution used for re-crystallisation were all shown to influence the nature of co-crystalline materials obtained. It was shown that the form in which glucose re-crystallised could be controlled by varying the conditions used. The co-crystallisation studies of sucrose and glucose encompassed mixtures which of each of the components being in the majority. For this purpose, the co-crystallisation process was accordingly adapted to glucose being main ingredient. In the case of glucose as the major component, the melting of glucose monohydrate was found to be the most efficient process. Glucose re-crystallised as a mixture of anhydrous α and β glucose. The ratio of which could be controlled by the temperature of re-crystallisation and the amount of sucrose incorporated. In both cases, either sucrose or glucose being the major component, a flowing agent was incorporated in the co-crystalline product and some of the materials prepared showed an improvement in the flowability over a dry blend comprising of a co-crystalline material and flowing agent. The phase diagram for the glucose-sucrose system was investigated using mixtures of the sugars which were physically ground together. A difference was found between materials which were ground together or separately. The system seemed to be eutectic. Nevertheless, as when the co-crystallisation process was applied, no new phase was observed on the X-ray diffraction patterns. The fact that glucose and sucrose did not belong to the same crystalline group (orthorhombic and monoclinic respectively) could explain why this system does not present a co-crystalline phase.

6.6. References

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CHAPTER VII

HYDRATED FORM OF SUCROSE

7.1. Aim

Crystalline sucrose at room temperature is anhydrous and melts at 186-192°C.[1] Nevertheless, crystalline hydrates of sucrose have been isolated during the study of the water-sucrose phase diagram.[2] These crystals were formed only at -34/-15°C and had melting points of 45.7 and 27.8°C respectively. Furthermore, inclusions of syrup have been observed in large crystals of sugar.[3] Even though crystals with major syrup inclusions were said to be more reactive, rapid dissolving and readily crushed,[4] no melting points were given for such crystals.

In solution, sucrose is surrounded by seven molecules of water in its hydration shell.[5] In concentrated solutions, the presence of a water bridge between the glucose and the fructose moieties has been proposed on the basis of molecular dynamic simulation.[6,7] This water bridged form was predicted to be in high population in aqueous solution and the bound water bridge molecule was believed to be the last to be removed before incorporation of the sucrose molecule in the crystal lattice. This hypothesis could explain the large metastable zone observed for sucrose.[8] Even though such hydrates present in aqueous solution have not been observed in the crystalline state; it supports the affinity of sucrose for water.

In the previous chapters on co-crystallisation, an extra peak at 150.7 to 152.2°C was observed on the DSC scans of the materials prepared. For the purpose of consistency and convenience in this chapter, this observation will be denoted as the peak at ca.

150°C. Similarly, the peak associated with the melting of anhydrous sucrose will be denoted as the peak at ca. 190°C. The peak at ca. 150°C could not be explained by the second ingredient added during the process of co-crystallisation or by the formation of a new phase resulting from a mixture of the constituents. Therefore, such a phase would appear to be due to a form of sucrose. The differences of melting in commercial sucrose have been observed by DSC.[9] In a recent paper,[10] it was proposed that such a peak appearing in the DSC traces was due to the devitrification of amorphous matter at the surface of the sucrose crystals. It was thus the aim in this work to undertake a systematic investigation of the conditions required to isolate and fully characterise this phase in a pure form.

7.2. Factors influencing the intensity of the peak at ca. 150°C relative to that of the peak at 190°C for sucrose observed by DSC

7.2.1. Purity of the materials

7.2.1.1. Re-crystallisation of different sugars

Sugars from different commercial sources were examined for their capacity to show the early melting peak at ca. 150°C by DSC analysis. These sugars namely, analytical grade sucrose from Fisher Chemicals, granulated sucrose from a random selection of commercial sources including, Tate and Lyle, Lancaster and Silver Spoon were re-crystallised by boiling an aqueous solution of sugar and allowing it to crystallise spontaneously on cooling (Method 9.6.1). The curves obtained by DSC analysis for the parent sugars are presented in Figure 7.1 and the data are recorded in Table 7.1. The DSC results for the re-crystallised sugars are shown in Figure 7.2 and Table 7.2.

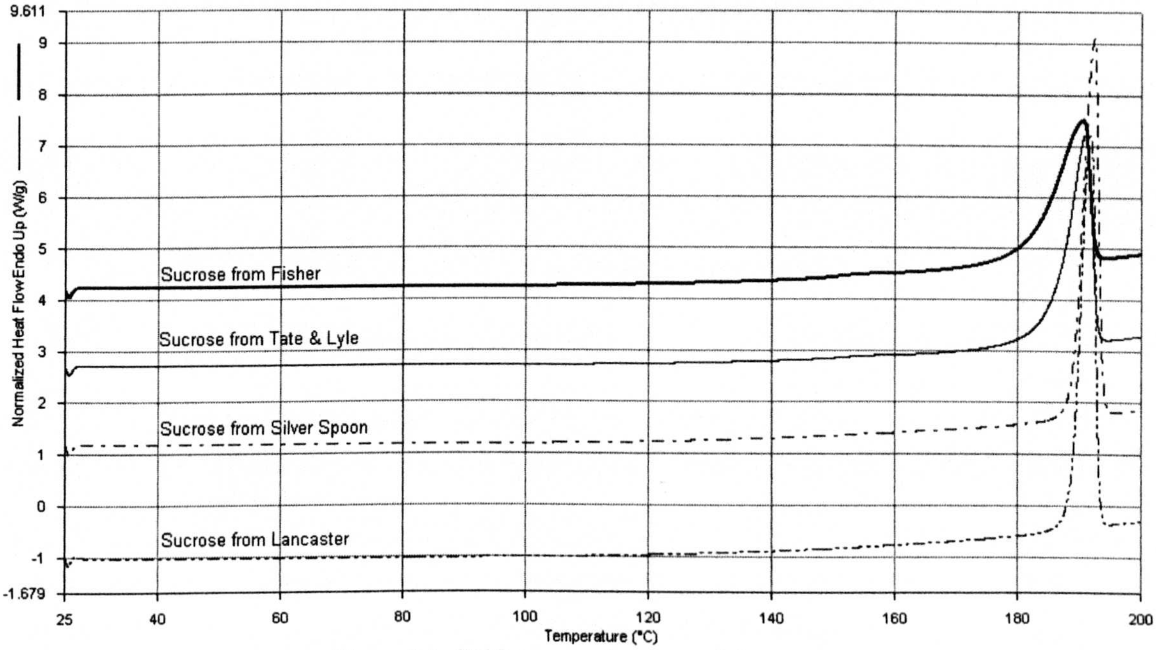

Figure 7.1: DSC traces of commercial sugars

Sucrose	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
Fisher Chemicals	154.3	190.5	1.1	116.0
Tate & Lyle	154.4	190.9	0.9	122.0
Silver Spoon	_	192.4	_	131.4
Lancaster	_	191.7	_	132.8

Table 7.2: DSC results of commercial sugars

It can be observed that both sugars from Silver Spoon and Lancaster showed a single peak at 192 ± 1°C. In contrast, the sugars from Tate & Lyle and Fisher Chemicals exhibited a peak at 154°C. Their second peak had a slightly lower melting point and enthalpy.

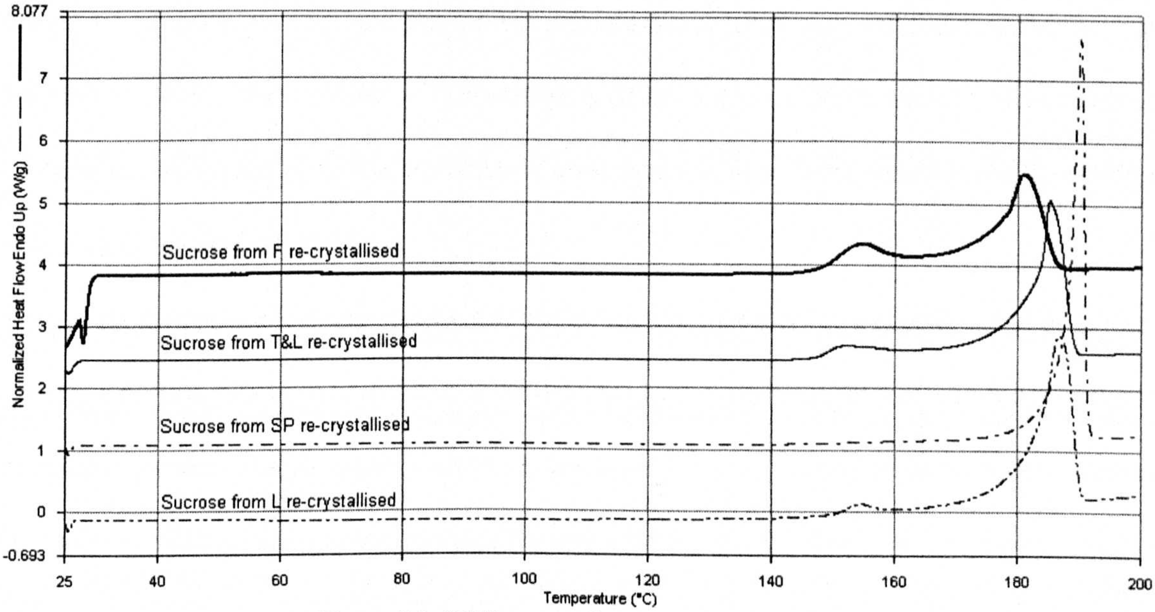

Figure 7.2: DSC traces of re-crystallised sugars

Sucrose	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
Fisher Chemicals	154.8	180.8	33.3	85.4
Tate & Lyle	152.2	185.2	17.1	101.0
Silver Spoon	–	190.0	–	119.3
Lancaster	154.3	186.8	3.9	108.5

Table 7.2: DSC results of re-crystallised sugars

When the sugars are re-crystallised, it is notable (Table 7.2) that in the Silver Spoon case, no peak at ca. 150°C was observed whereas the second melting was the highest of the three samples examined. The second melting temperature diminished in the order SP > L>T&L > FC. The intensity of the first melting peak increased in the same order.

7.2.1.2. Purity analyses

The DSC scans of the sucrose from Fisher Chemicals and the sucrose from Tate & Lyle are similar to that which would be expected if an impurity were to be present in the sucrose crystals. The purity of the three sugars was thus determined. HPLC was used to detect any organic impurities in the samples of sucrose. It was thought that perhaps traces of glucose or fructose might be present since they can be formed during the boiling of the sucrose solutions by hydrolysis of the sucrose. Nevertheless, the presence of such invert sugars or any other organic compounds could be detected in neither of the sugar samples investigated.

Such a result focused attention towards the possible presence of mineral salt impurities. Indeed, such minerals as sodium, potassium and low concentrations of sulphates are not completely removable by clarification of the sugar juices.[11] Such are usually determined in sucrose solutions as part of the quality control process in factories by analysis of the colour and the ash content.[12] The first parameter is measured by spectrophotometric analysis.[13] Solutions of sugar containing a large amount of mineral salts normally exhibit a yellowish coloration. Such spectrophotometric analyses are normally undertaken at 420 nm. The values of the absorbance of the solutions (Method 9.7.8) are shown in Table 7.3. Fisher Chemicals sucrose gave the lowest value (0.0505) for the absorbance at 420 nm, whereas the sucrose from Silver Spoon gave the highest value. These results indicate that the sucrose from Fisher Chemicals contains the least amount of mineral salts of the three and Silver Spoon the highest. Such a result is not surprising since sucrose from Tate and Lyle is obtained from sugar cane (*Saccharum officinarum*) whereas sucrose from Silver Spoon is obtained from sugar beet (*Beta vulgaris*). Sugar beets are known to be maritime plants[14] and by their nature to absorb more minerals than sugar derived from sugar cane.

Material	Absorbance E_{420}
Fisher Chemicals	0.0505
Lancaster	0.0610
Tate & Lyle	0.0599
Silver Spoon	0.0574

Table 7.3: Absorbance values of commercial sugar solutions

The ash content was determined by measurement of the conductivity of the solutions of sucrose.[15] The conductivity values are shown in Table 7.4. As might be expected, the sucrose solution from Fisher Chemicals gave the lowest conductivity value and the sucrose from Silver Spoon gave the highest. Both the conductivity measurements and spectrophotometric analysis were in agreement in identifying relative amounts of mineral salts. Thus, it would appear that the presence of such salts inhibits the formation of the first melting peak at 150°C during crystallisation.

Sample	Conductivity (μS.cm^{-1})	Temperature (°C)
Purified water	1.97	21.2
Fisher Chemicals	3.32	21.4
Lancaster	16.27	22.8
Tate & Lyle	15.90	22.5
Silver Spoon	17.98	22.6

Table 7.4: Conductivity values of commercial sugar solutions

Flame photometry was used to quantify the amount of cations present in the sucrose samples. The results of atomic absorption spectrophotometry are shown in Table 7.5. Both sodium and potassium concentrations determined for the sucrose from Silver Spoon were found to be some 17 fold higher than in Fisher Chemicals.

Sucrose	Concentration of Na (ppm)	Concentration of K (ppm)
Silver Spoon	4.0	26.0
Fisher Chemicals	0.2	1.5

Table 7.5: Concentration of sodium and potassium in the sugars

The presence of impurities appears to be contrary to that expected whereby a lower melting point is found for the purer sugars. It can be concluded, therefore that there is a link between the concentration of mineral salts and the intensity of the first melting peak at ca. 150°C.

7.2.1.3. Removal of the mineral salts

- Successive re-crystallisations

In order to confirm this observation, a high ash sugar (Tate and Lyle) was re-crystallised three times from aqueous sugar solutions (85%) which were boiled at 128°C. The purified crystals were obtained by centrifugal filtration. DSC (Figure 7.3) and conductivity measurements (Table 7.6) were taken for each fractional crystallisation.

Product	Conductivity (μS.cm^{-1})	Temperature (°C)
High ash sucrose	23.90	19.7
High ash sucrose after 1st re-crystallisation (filtered)	13.76	19.9
High ash sucrose after 2nd re-crystallisation (filtered)	14.09	19.9
High ash sucrose after 3rd re-crystallisation (filtered)	13.81	19.9

Table 7.6: Conductivity values of the sugars after successive re-crystallisations

The conductivity of solutions made up from the re-crystallised fractions was found to be significantly lower than those made up from each parent sugar indicating a depletion of mineral salts. Surprisingly, the value for the second re-crystallisation fraction was higher than that obtained from the first re-crystallisation which might be due to the deionised water containing some inorganic impurities.

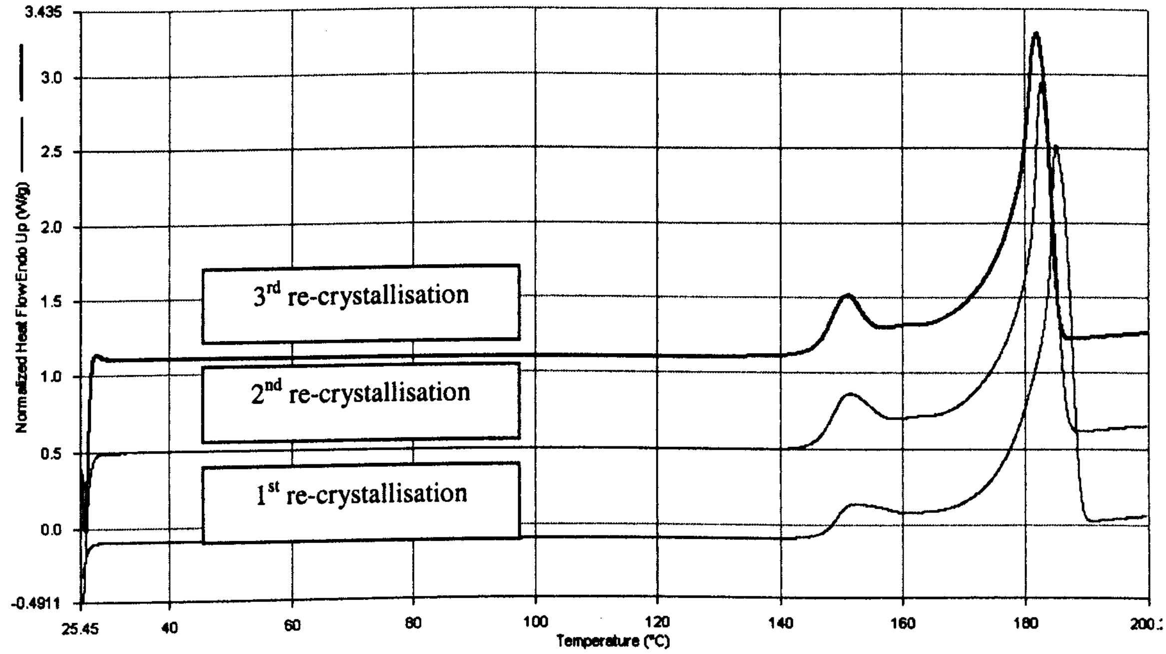

Figure 7.3: DSC traces of the sugars after successive re-crystallisations

Material	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
High ash sucrose 1st re-crystallisation	152.2	185.2	17.1	101.0
High ash sucrose 2nd re-crystallisation	151.5	182.7	22.0	94.5
High ash sucrose 3rd re-crystallisation	151.0	182.1	22.3	91.8

Table 7.7: DSC results of the sugars after successive re-crystallisations

With each re-crystallisation the peak intensity at ca. 150°C increased: 14.49%, first re-crystallisation; 18.91%, second; 19.81%, third. The difference in intensity of the peak at ca. 150°C between the first and the second re-crystallisation products is more significant than that between the second and the third re-crystallisation products. Such results indicate that only marginal improvements in purity can be achieved by re-crystallisation. It should be noted that successive re-crystallisations in water can lead to the formation of invert sugar.

- Purification by ion exchange column

A solution of high ash sucrose (Silver Spoon) was passed through an ion exchange resin (50 g of monobed resin in a column of 2.5 cm of diameter). The conductivity of the solutions was measured before and after passing through the resin (Table 7.8). The purified solution from the high ash sugar (Silver Spoon) yielded crystals whose DSC melting characteristics are presented in Figure 7.4 and Table 7.9.

Material	Conductivity (μS.cm^{-1})	Temperature (°C)
High ash sucrose solution (28%) before passage on resin	24.50	26.5
High ash sucrose solution (28%) after passage on resin	9.32	23.6

Table 7.8: Conductivity value of the high ash sucrose solution before and after purification on ion exchange column

Table 7.8 shows that the conductivity of the solution decreased after a passage through the ion exchange resin indicating that a large proportion of the mineral salts was removed.

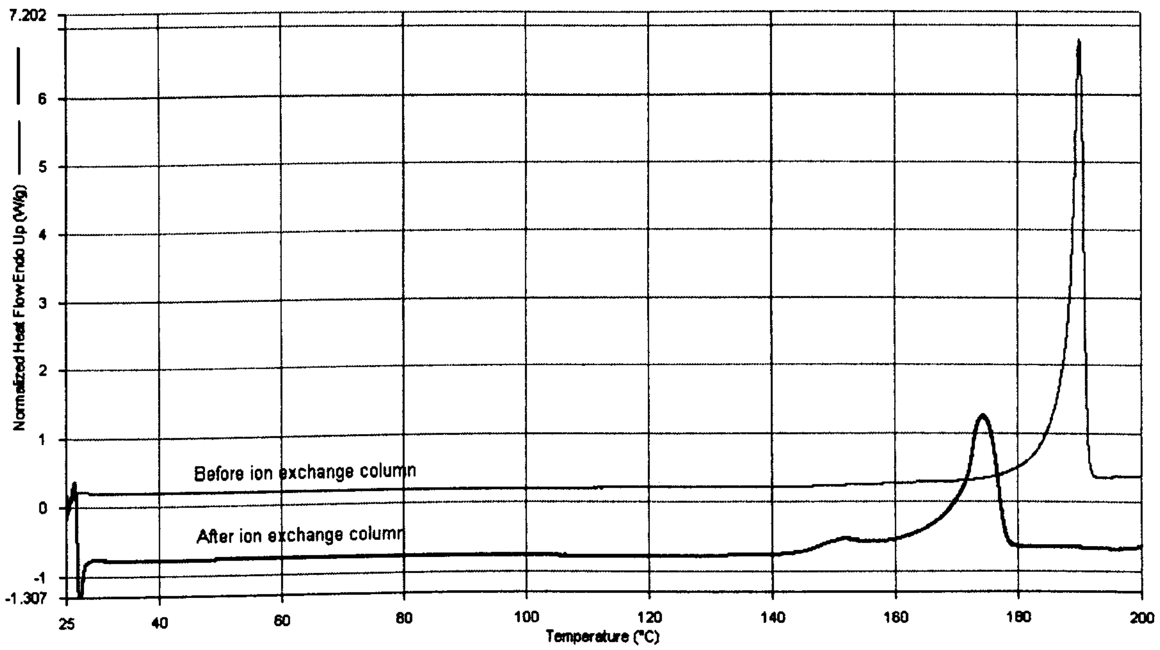

Figure 7.4: DSC traces of the high ash sucrose before and after purification on ion exchange column

Material	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
Before ion exchange treatment	–	190.0	–	119.3
After ion exchange treatment	151.9	174.3	13.9	81.0

Table 7.9: DSC results of the high ash sucrose before and after purification on ion exchange column

Figure 7.4 and Table 7.9 show the differences obtained by DSC between a re-crystallised high ash sucrose that has not been passed through an ion exchange resin and the same sucrose re-crystallised after purification by the resin. Either purification by successive re-crystallisations or treatment with an ion exchange resin produce a peak at ca. 150°C which is consistent with lower conductivity measurements and hence lower amounts of mineral salts impurities.

7.2.1.4. Addition of mineral salts

To explore more thoroughly this phenomenon, it was envisaged that the addition of a mineral salt such as potassium chloride, which is one of the impurities contained in commercial sucrose, to a sugar showing the peak at ca. 150°C, should cause its disappearance. The peak at 150°C is well pronounced in the low ash sucrose obtained from Fisher Chemicals. Therefore, this sugar was contaminated by re-crystallising it in presence of different amounts of potassium chloride.

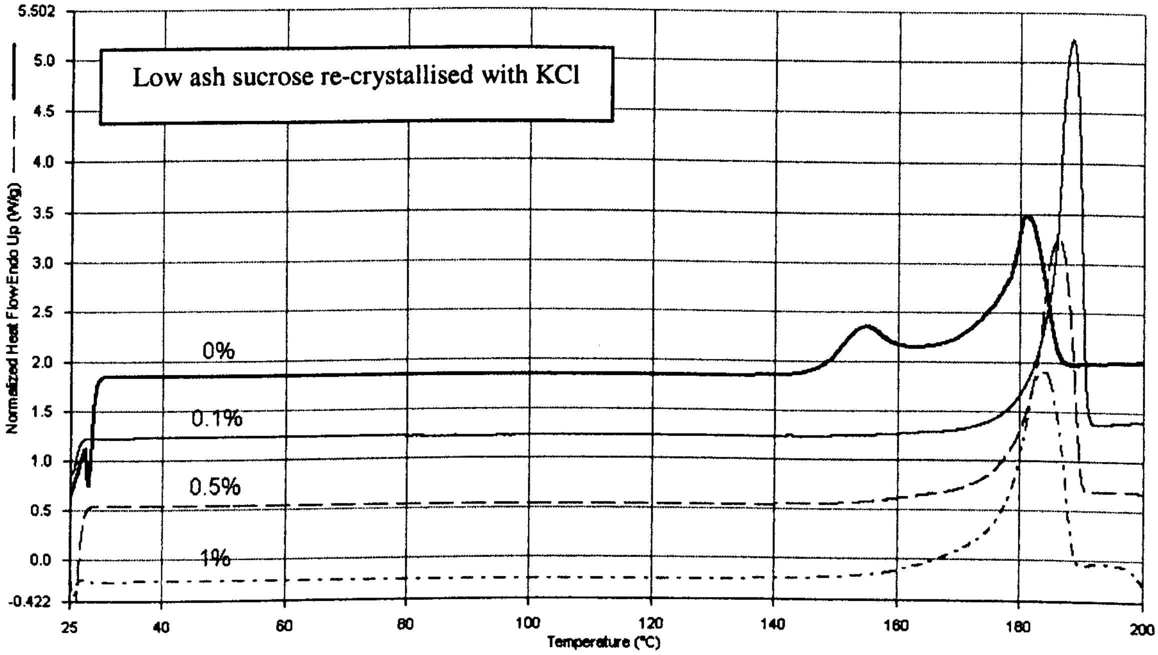

Figure 7.5: DSC traces of the low ash sucrose re-crystallised in presence of potassium chloride

% KCl	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
0	154.8	180.8	33.3	85.4
0.1	_	188.4	_	119.8
0.5	_	186.1	_	110.0
1	_	184.1	_	112.6

Table 7.10: DSC results of the low ash sucrose re-crystallised in presence of potassium chloride

It was found that the peak at 150°C completely disappeared with sugars re-crystallised from as little as 0.1% of potassium chloride solutions (Figure 7.5; Table 7.10). It was noted that higher concentrations resulted in the melting peak of sucrose appearing at a lower temperature and becoming broader with its enthalpy decreasing. Parallel experiments in which either NaCl or K_2SO_4 replaced KCl showed similar disappearance of the peak at ca. 150°C (Figure 7.6; Table 7.11 and Figure 7.7; Table 7.12 respectively)

Re-crystallisations using increased concentrations of sodium chloride solutions similarly resulted in a decrease in the enthalpy and the melting point of sucrose.

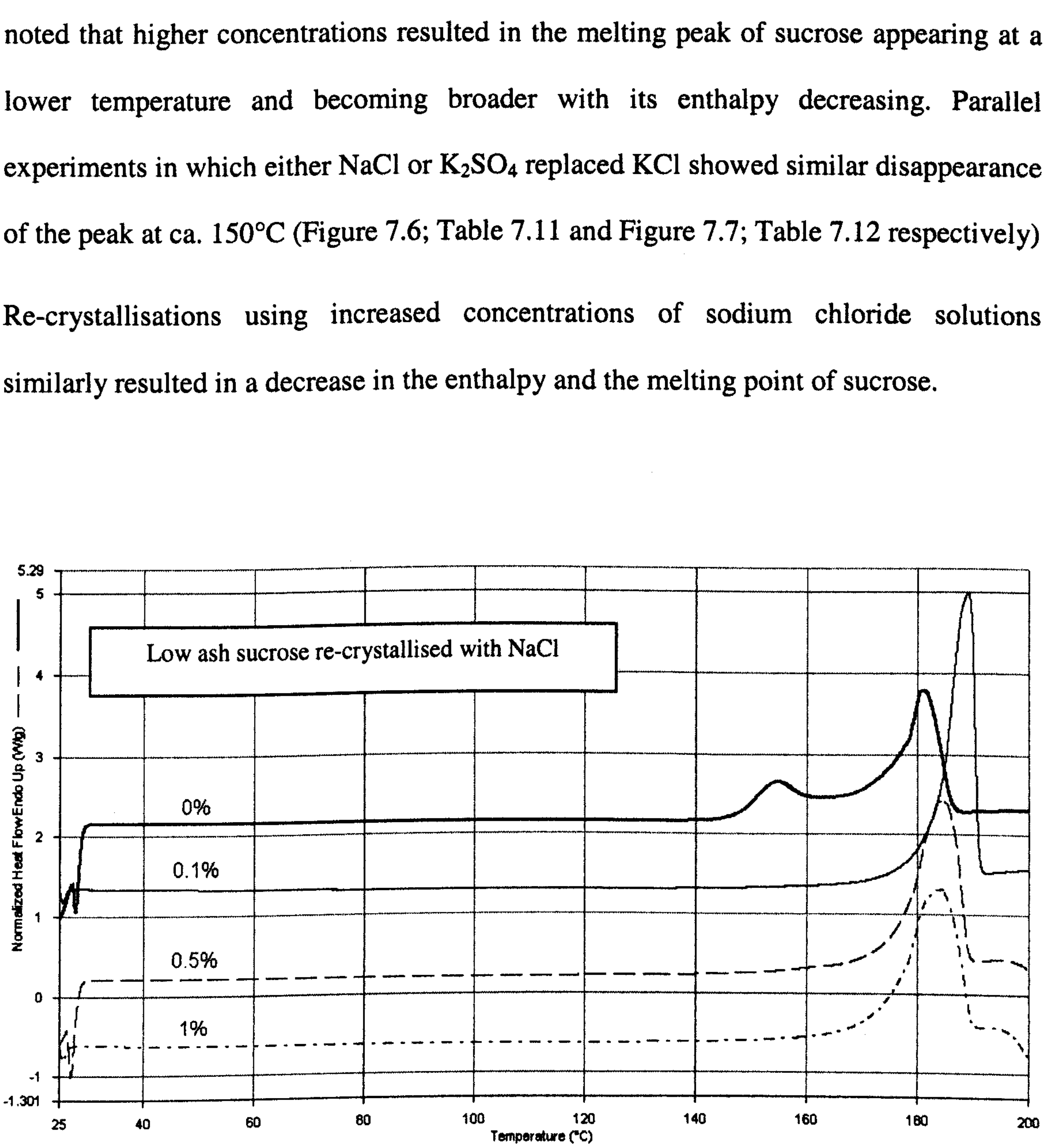

Figure 7.6: DSC traces of the low ash sucrose re-crystallised in presence of sodium chloride

% NaCl	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
0	154.8	180.8	33.3	85.4
0.1	_	189.1	_	122.7
0.5	_	183.8	_	111.0
1	_	184.3	_	112.5

Table 7.11: DSC results of the low ash sucrose re-crystallised in presence of sodium chloride

Up to 0.1% of mineral salts (KCl and NaCl), their presence inhibits the formation of the phase melting at ca. 150°C and there is a single melting peak for sucrose. Above this concentration, the mineral salts still inhibit the peak at ca. 150 but the extra salts act as an impurity for normal sucrose crystallisation and the temperature of the second melting peak decreases.

In contrast, re-crystallisation with increasing potassium sulphate concentrations above 0.1% did not decrease either the melting point or the enthalpy of sucrose melting in the range of concentrations studied.

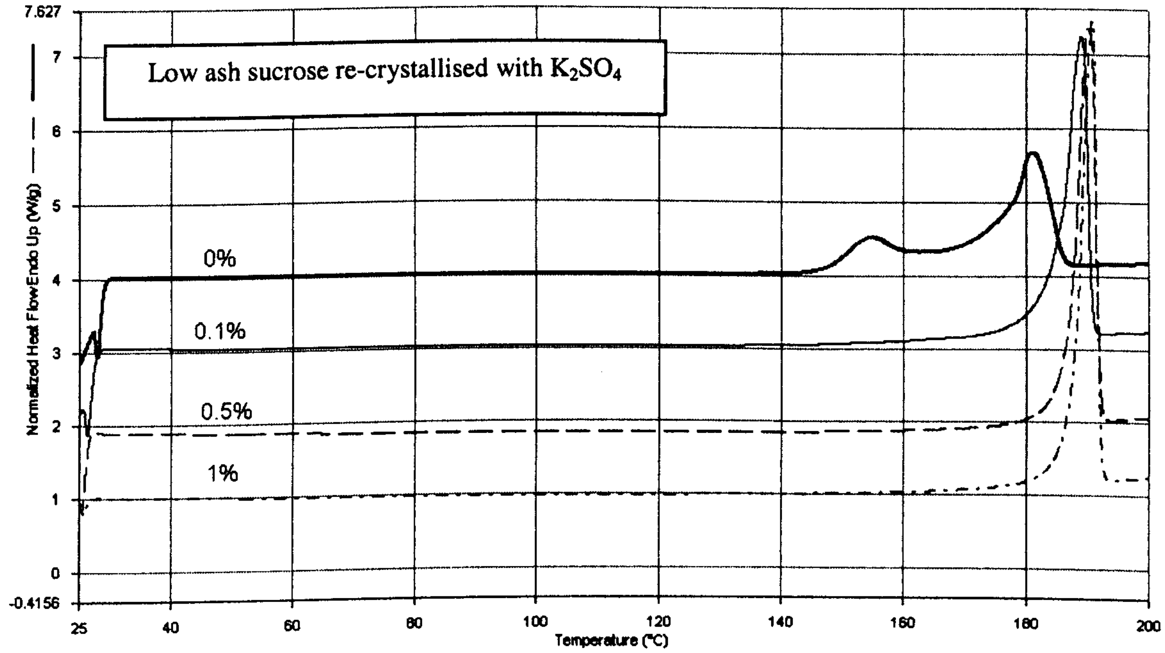

Figure 7.7: DSC traces of the low ash sucrose re-crystallised in presence of potassium sulphate

% K_2SO_4	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
0	154.8	180.8	33.3	85.4
0.1	_	189.0	_	117.7
0.5	_	190.1	_	125.2
1	_	190.8	_	124.5

Table 7.12: DSC results of the low ash sucrose re-crystallised in presence of potassium sulphate

Figure 7.8 shows the DSC scans of a low ash sucrose re-crystallised in purified water and in tap water (prescribed concentration for tap water: 150 mg Na/L, 12 mg K/L).[16] The values for enthalpy and melting temperatures are given in Table 7.13. Re-crystallisation of sucrose from tap water resulted in the disappearance of the peak at 150°C. Table 7.14 shows the conductivity values for the two types of water used in the experiment.

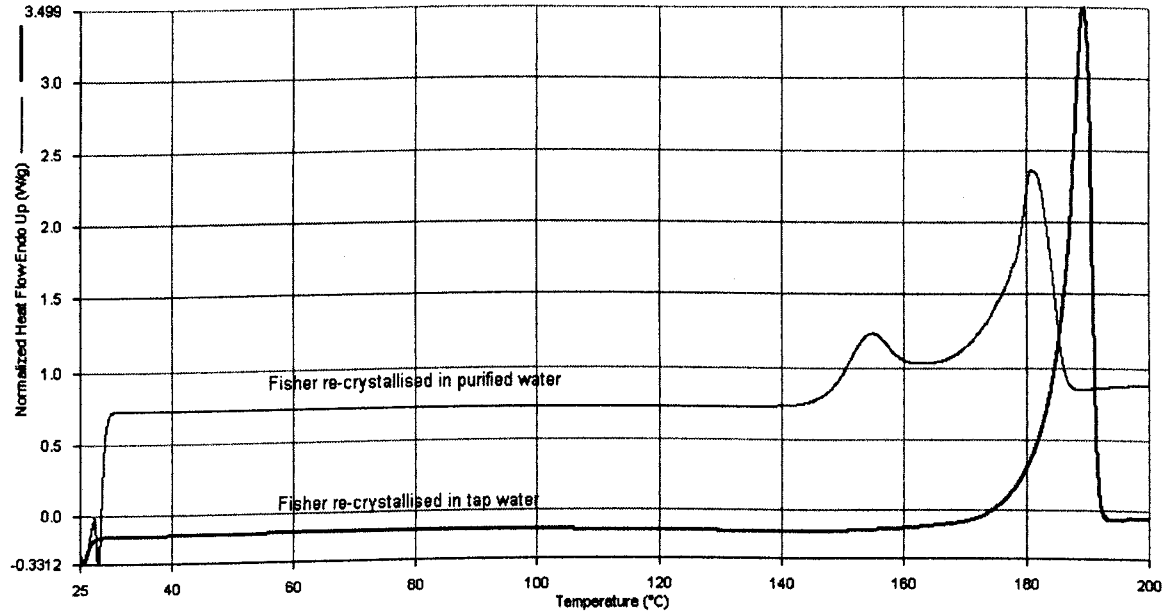

Figure 7.8: DSC traces of the low ash sucrose re-crystallised in tap water

Material	T1(°C)	T2(°C)	ΔH1(J/g)	ΔH2(J/g)
Low ash sucrose re-crystallised in purified water	154.8	180.8	33.3	85.4
Low ash sucrose re-crystallised in tap water	–	189.4	–	122.3

Table 7.13: DSC results of the low ash sucrose re-crystallised in tap water

Sample	Conductivity ($\mu S.cm^{-1}$)	Temperature (°C)
Purified water	2.20	17.8
Tap water	644.00	17.6

Table 7.14: Conductivity values of tap and purified water

It can be concluded that the addition or removal of minerals salts from sucrose can alter its thermal profile such that the presence of mineral salts induce a sole melting peak in the range 180-190°C. In contrast, in the absence of mineral salts an additional peak emerges in the range 151-154°C. It is known that the degradation of sucrose is hindered by the presence of inorganic salts.[17] The re-crystallised low ash and high ash sugars (Method 9.6.1) were analysed by HPLC; the re-crystallised high ash sucrose show no trace of invert sugars whereas the low ash sucrose had an invert sugar content of 0.22%.

7.2.1.5. Addition of other types of impurities

Several possibilities for the explanation of this phase arise. This early melting peak could be due to the formation of a hydrate of sucrose[18], the inclusion of mother liquor in the crystal lattice or again the presence of amorphous matter at the surface of the crystals as suggested in a recent paper.[10]

The influence of mineral salts on the thermal properties of crystalline sucrose has been found significant. In contrast, it has been seen in Chapter 5 that the addition of the monosaccharide sugars from honey in the concentration 0-20% had little influence on the temperature and area of the extra peak at ca. 150°C. If the phase was due to the inclusion of water, the proportion of the peak at ca. 150°C would be influenced by the type of impurity added and its interaction with water. Thus, other organic substances were explored in an attempt to understand better the reasons for the appearance of this phase. Two aprotic solvents, DMF and DMSO, along with two carbohydrates, spray dried glucose syrup GL01934® and maltodextrin MD01915® were added to the sucrose solution prior to re-crystallisation.

DSC traces with increasing amounts of a second ingredient are shown in Figures 7.9., 7.10, 7.11, 7.12 and 7.13 for the mixtures: low ash sucrose-GL01934®; high ash sucrose-GL01934®; low ash sucrose-MD01915®; low ash sucrose-DMF; low ash sucrose-DMSO respectively. DMF showed the strongest influence (Figure 7.12) on the peak at 150°C by making it disappear by a proportion of 10%. The presence of DMSO (Figure 7.13) gave bumpy base lines. The low ash sucrose-GL01934® mixtures gave the peak at 150°C with the highest intensities.

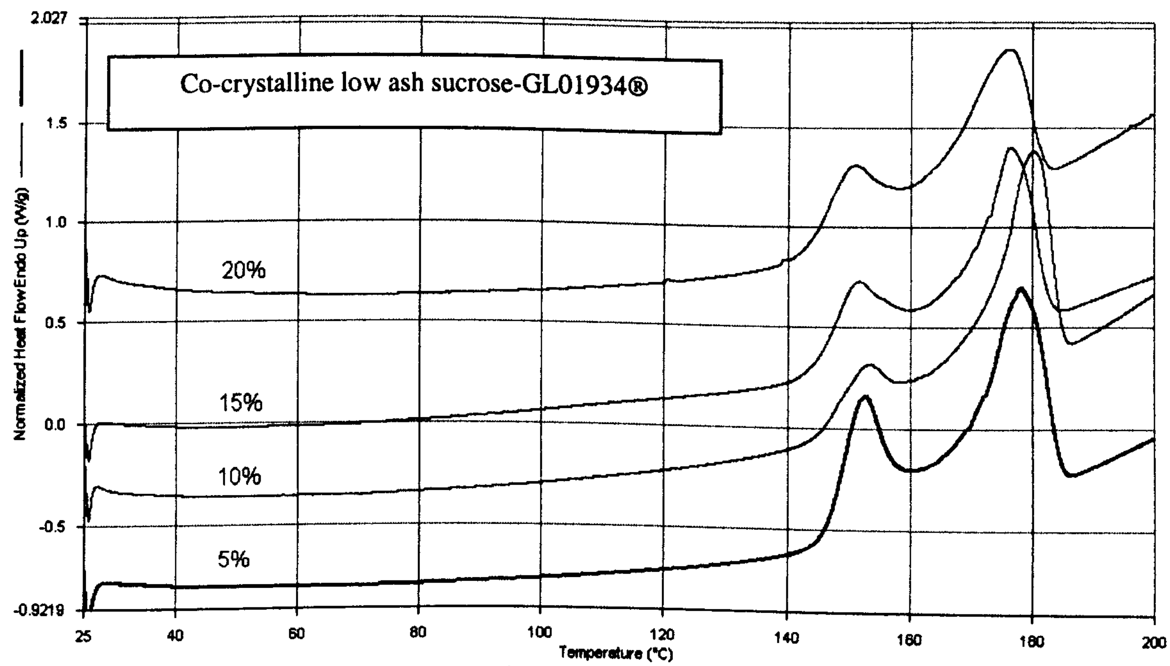

Figure 7.9: DSC traces of the low ash sucrose re-crystallised in presence of GL01934®

% GL01934®	T1(°C)	T2(°C)	ΔT(°C)	ΔH1(J/g)	ΔH2(J/g)	ΔHT(J/g)
5	152.7	178.2	25.5	47.8	56.8	104.6
10	153.4	180.2	26.8	25.7	56.0	81.7
15	151.6	176.4	24.7	37.9	45.9	83.7
20	151.0	176.2	25.2	40.8	40.9	81.7

Table 7.15: DSC results of the low ash sucrose re-crystallised in presence of GL01934®

The results for the addition of the glucose syrup GL01934® to a low ash sucrose (Figure 7.9) are in agreement with the inclusion of water. The glucose syrup is competing for the water with sucrose. Thus, an increase in glucose syrup decreases the enthalpy of the peak at ca. 150°C.

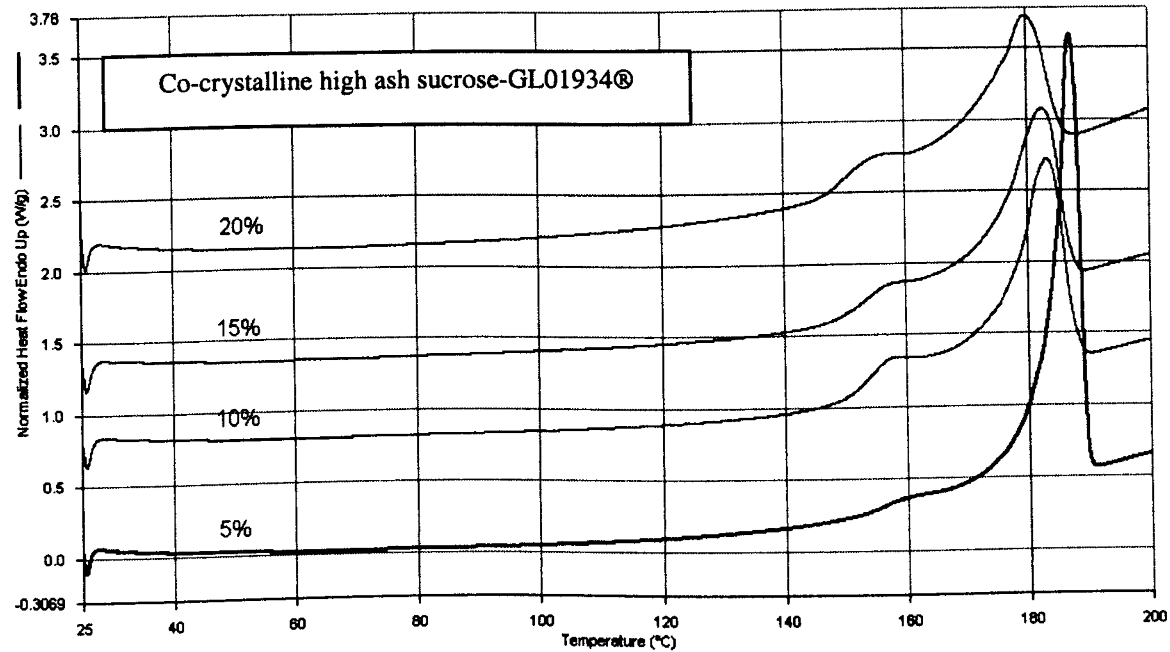

Figure 7.10: DSC traces of the high ash sucrose re-crystallised in presence of GL01934®

% GL01934®	T1(°C)	T2(°C)	ΔT(°C)	ΔH1(J/g)	ΔH2(J/g)	ΔHT(J/g)
5	159.4	187.2	27.7	0.9	101.6	102.4
10	157.1	183.3	26.1	5.1	72.0	77.1
15	156.7	182.5	25.9	2.3	67.2	69.5
20	154.4	180.0	25.5	4.7	52.7	57.3

Table 7.16: DSC results of the high ash sucrose re-crystallised in presence of GL01934®

With a high ash sucrose (Figure 7.10), the increase in the glucose syrup amount, increases the intensity of the first melting peak. This could be due to the formation of polysaccharides-mineral salts clusters releasing the water molecules which were clustered around the mineral salts before the addition of the spray dried glucose syrup.

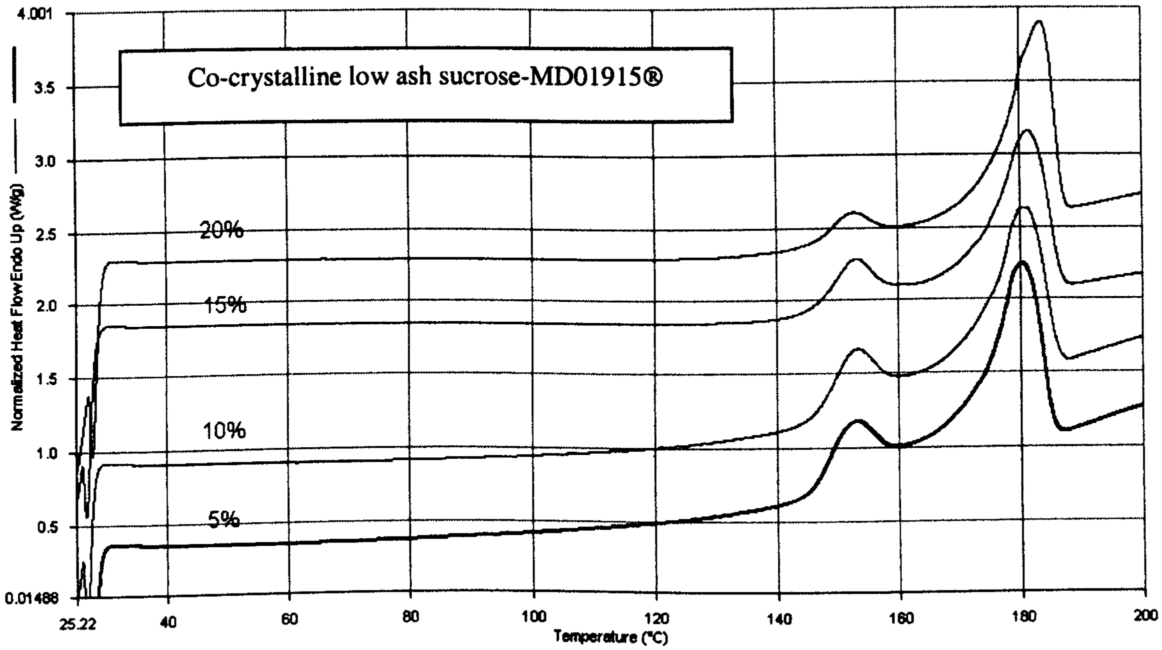

Figure 7.11: DSC traces of the low ash sucrose re-crystallised in presence of MD01915®

% GL01915®	T1(°C)	T2(°C)	ΔT(°C)	ΔH1(J/g)	ΔH2(J/g)	ΔHT(J/g)
5	151.2	180.3	29.1	36.8	65.7	102.4
10	153.3	180.6	27.3	37.6	62.2	99.8
15	153.1	181.6	28.4	29.0	61.6	90.6
20	152.7	183.5	30.7	18.6	62.6	91.2

Table 7.17: DSC results of the low ash sucrose re-crystallised in presence of MD01915®

As with the glucose syrup, with a low ash sucrose, the maltodextrin is taking up the water present, depleting the hydrated form of sucrose (Figure 7.11).

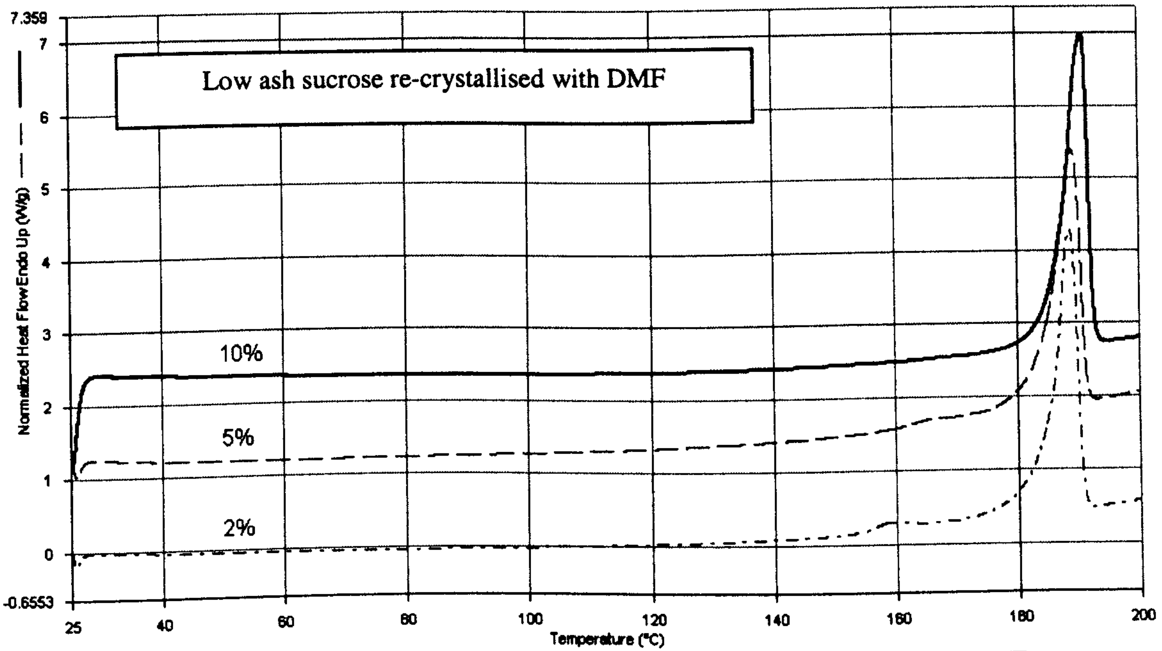

Figure 7.12: DSC traces of the low ash sucrose re-crystallised in presence of DMF

% DMF	T1(°C)	T2(°C)	ΔT(°C)	ΔH1(J/g)	ΔH2(J/g)	ΔHT(J/g)
2	158.9	188.6	29.7	3.2	111.2	114.5
5	166.0	189.1	23.1	1.5	110.8	112.3
10	–	190.9	–	–	122.5	122.5

Table 7.18: DSC results of the low ash sucrose re-crystallised in presence of DMF

As expected, the addition of increasing levels of DMF makes the first melting peak disappear (Figure 7.12). The higher polarity of DMF compared to polysaccharides results in a more significant effect on the proportion of the hydrated phase.

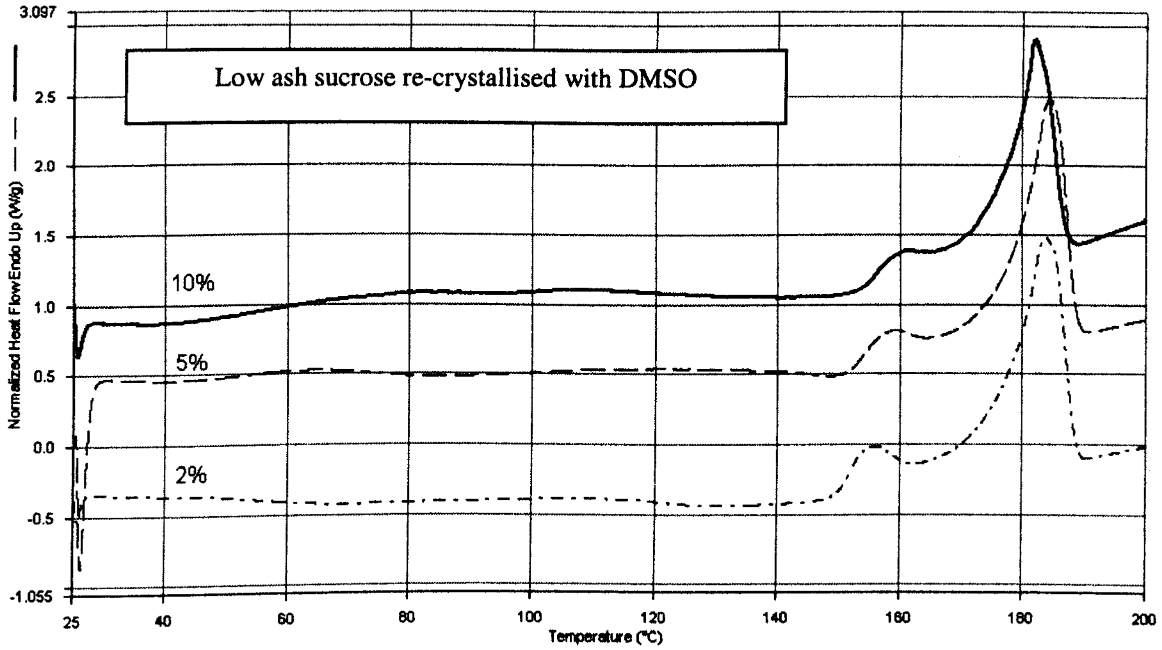

Figure 7.13: DSC traces of the low ash sucrose re-crystallised in presence of DMSO

% DMSO	T1(°C)	T2(°C)	ΔT(°C)	ΔH1(J/g)	ΔH2(J/g)	ΔHT(J/g)
2	156.1	183.8	27.7	22.6	88.0	110.6
5	159.4	184.3	24.9	18.3	83.6	101.9
10	160.8	181.9	21.2	16.7	68.4	85.1

Table 7.19: DSC results of the low ash sucrose re-crystallised in presence of DMSO

When DMSO, which is also a polar aprotic solvent, is added, the decrease in enthalpy of the first melting peak is less significant than with DMF but it can still be observed (Figure 7.13).

The evolution of the temperature of the first peak (T1) for the different mixtures is shown in Figure 7.14. For both DMF and DMSO, the increase of second ingredient increased T1 whereas it remained about the same when the proportion of maltodextrins was increased.

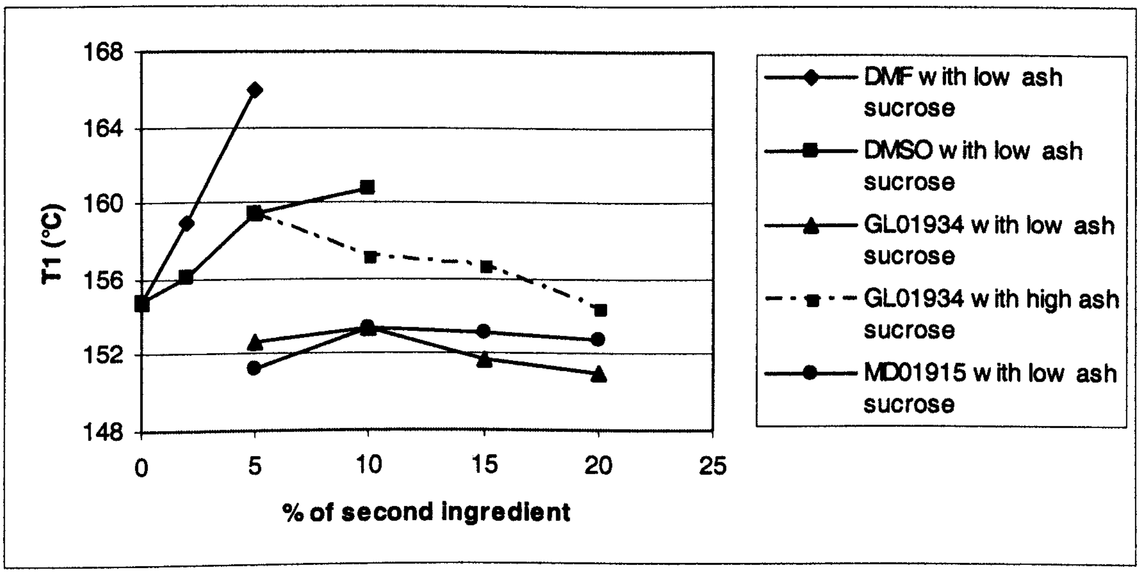

Figure 7.14: Evolution of T1 with increasing amount of second ingredient

The addition of DMF also increased the second melting peak (T2). On the contrary, the addition of GL01934® seemed to decrease it (Figure 7.15).

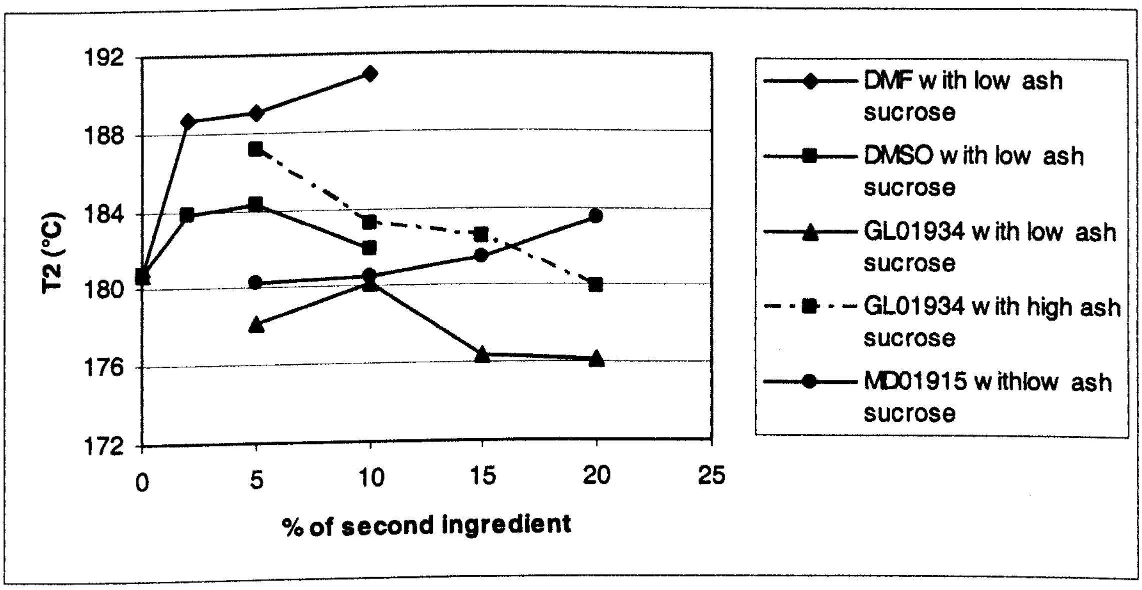

Figure 7.15: Evolution of T2 with increasing amount of second ingredient

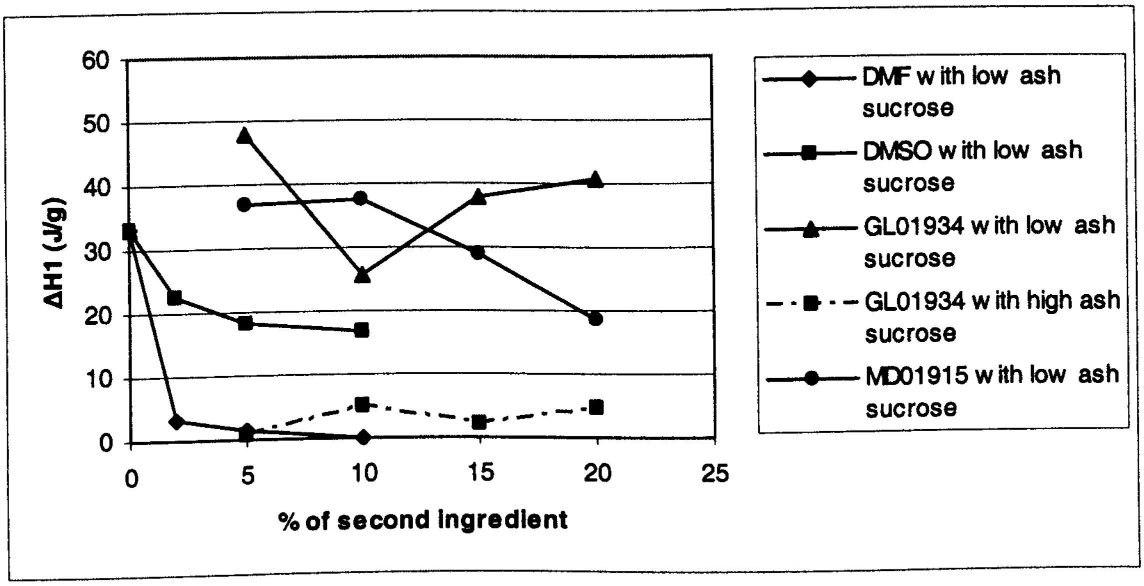

Figure 7.16: Evolution of ΔH1 with increasing amount of second ingredient

The enthalpy of the first peak was decreased by addition of DMF and DMSO, DMF having the strongest influence. The presence of only 2% of the solvents made the intensity of the first peak decrease sharply. Above this level the decrease in enthalpy was less important (Figure 7.16). The presence of the maltodextrin MD01915® also seemed to decrease the intensity of the first peak but the influence of the glucose syrup GL01934® was less distinct.

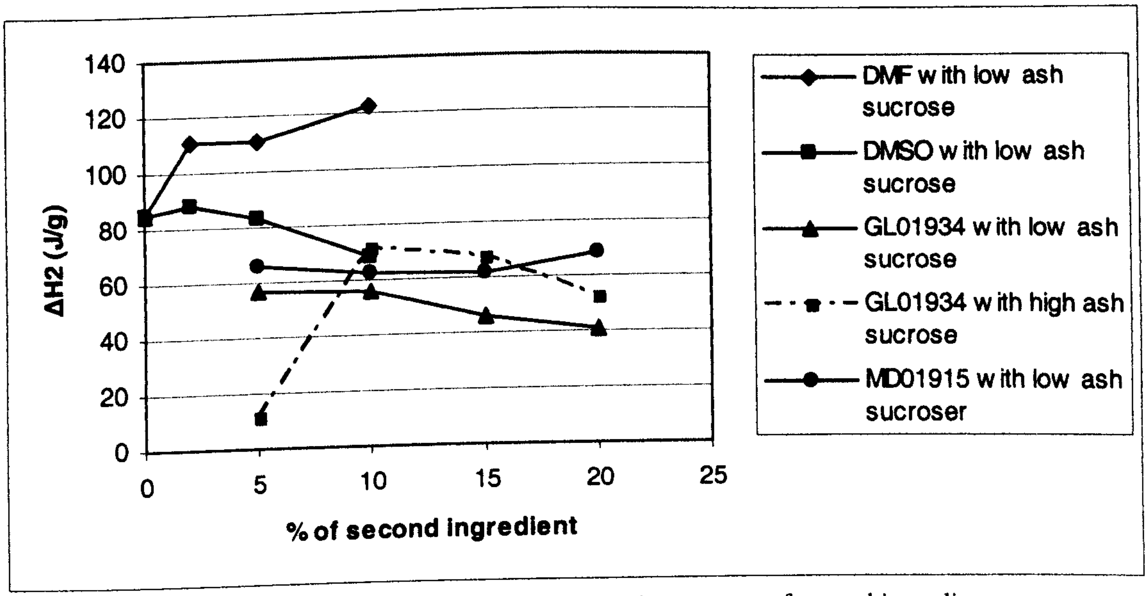

Figure 7.17: Evolution of ΔH2 with increasing amount of second ingredient

DMF and DMSO had different effects on the enthalpy of the second melting peak. The addition of DMF increased ΔH2 whereas the addition of DMSO decreased its intensity. Again the maltodextrins did not seem to have any effect on the enthalpy of the second peak (Figure 7.17).

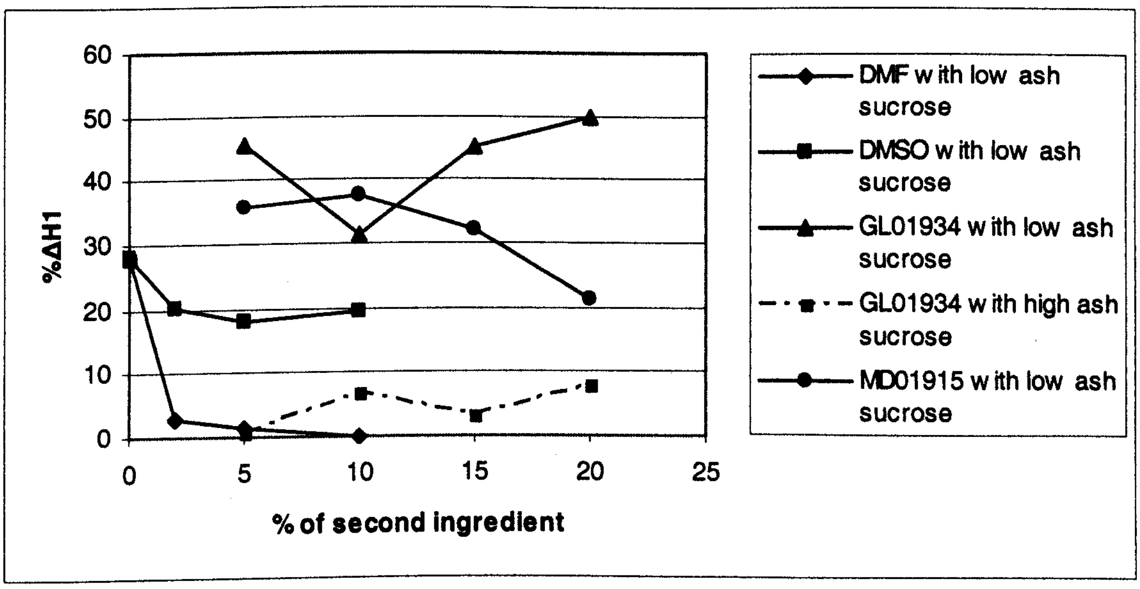

Figure 7.18: Evolution of the percentage of ΔH1 with increasing amount of second ingredient

The relative intensity of the first peak compared to the total melting enthalpy of sucrose followed the same trend than the evolution of its intensity. The effect of the addition of DMSO was less clear since its presence also decreased the intensity of the second melting peak (Figure 7.18).

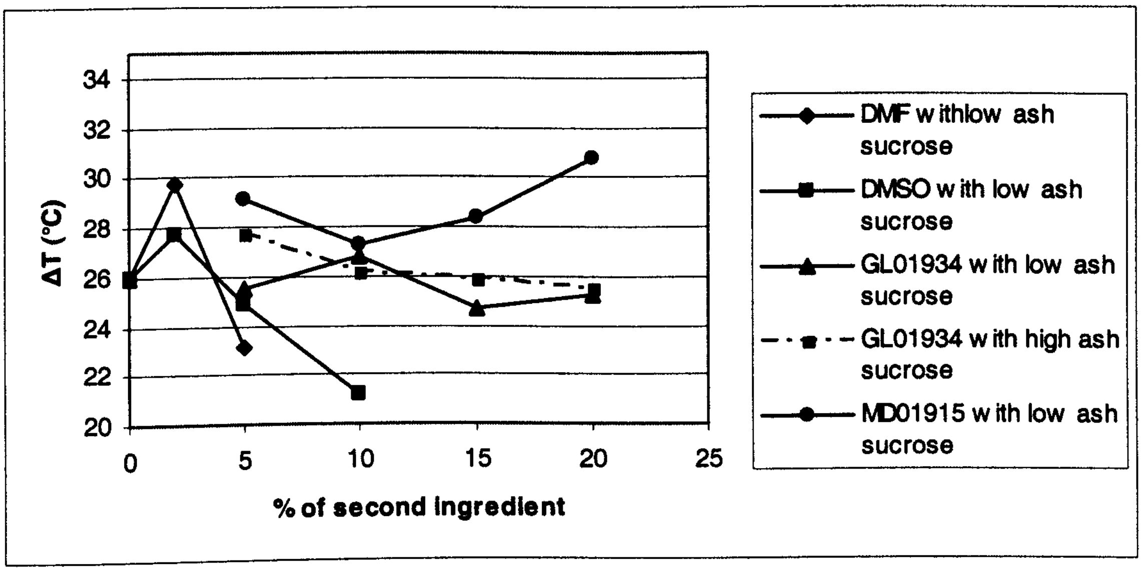

Figure 7.19: Evolution of T2-T1 with increasing amount of second ingredient

The increase of DMF and DMSO present in solution decreased the gap between the two peaks for the proportion 5 and 10%. The gap between the two peaks remained the same when increasing the proportion of glucose syrup and maltodextrin (Figure 7.19).

As for honey, the addition of polysaccharides did not have any significant effect on the peak at 150°C. On the contrary, the addition of a polar aprotic solvent did decrease the enthalpy of this peak, DMF having the strongest effect. This difference of behaviour between DMSO and DMF was not expected since both of them have similar dipolar moments, DMSO having the highest one.[19] The effect of the different impurities on the phase investigated can then be roughly ranked by the strength of their interactions with water. An impurity interacting mainly via hydrogen bonds is not very competitive compared to sucrose, whereas the mineral salts and to a lesser extent polar aprotic solvents have much stronger interactions with water. Clusters of water can form around minerals salts. Around ions, a hydration shell is formed whose density increases with increase of concentration.[20] The hydration number for sodium was found to be 5 or 6 water molecules,[21,22] whereas the hydration number of potassium was found to have a probability distribution ranging from 5 to10.[21] Strong interactions between water and ions orient spatially water molecules in hydration shell that in turn results in spatial arrangement of neighbouring water molecules. In effect, the ions are surrounded by few layers of oriented spatially water molecules.[20] In addition, clusters of the types 1 DMSO-2 H_2O and 1 DMSO-3 H_2O were found by molecular dynamic simulations[23] and DMF-2 H_2O complexes were indicated by viscosity and dielectric constant measurements.[24,25] Water seems then to be at the origin of the phenomenon, since when it was less available to perturb the crystallisation of sucrose, the first melting peak at 150°C decreased or completely disappeared.

7.2.2. *Influence of the level of supersaturation*

A low ash sucrose (Fisher Chemicals) and high ash sucrose (Tate & Lyle) were used to be re-crystallised at different temperatures. Figure 7.20 shows the proportion of first peak depending on the boiling temperature. One can see that the proportion of first peak decreased when the boiling temperature of the sucrose solution was increased. When centrifugation is applied later on the crystals, the enthalpy of the first peak decreased slightly. Furthermore, whatever the temperature used, the proportion of first peak is consistently higher when using the low ash sucrose.

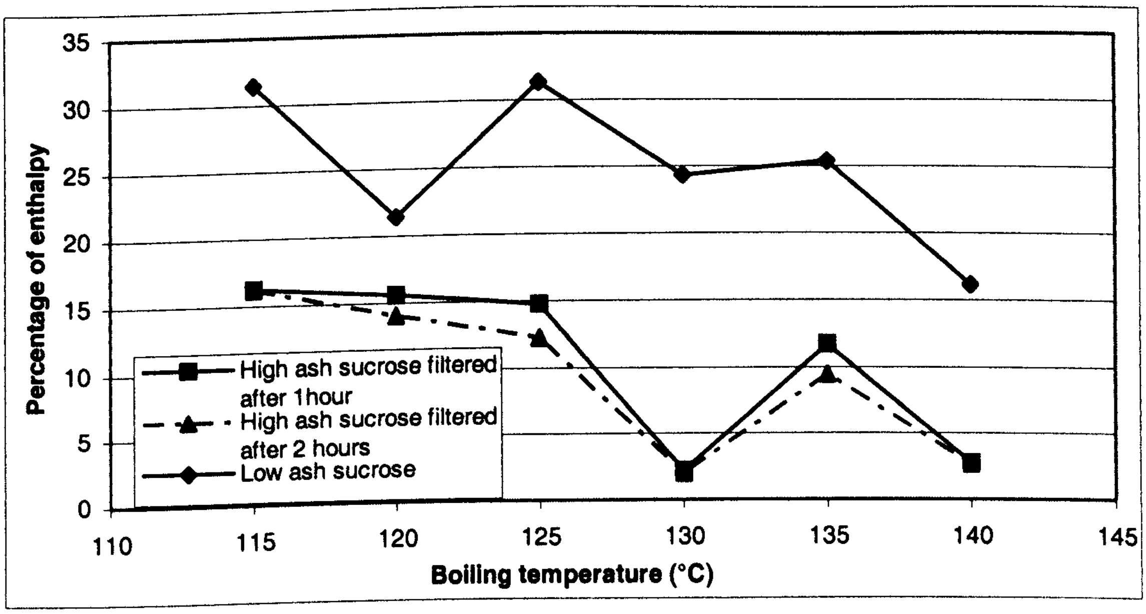

Figure 7.20: Evolution of the percentage of ΔH1 with increasing boiling temperature

Figure 7.21 shows the evolution of the difference between the onset temperatures of the two peaks when the boiling temperature of the sucrose solution was increased. The higher the boiling temperature was, the more distinct the peaks were.

The level of supersaturation had then a marked effect on the enthalpy of the phase. By increasing the level of supersaturation, the amount of water present decreased. This shows once more that the amount of water available during the re-crystallisation plays a role in the obtaining of the first melting peak.

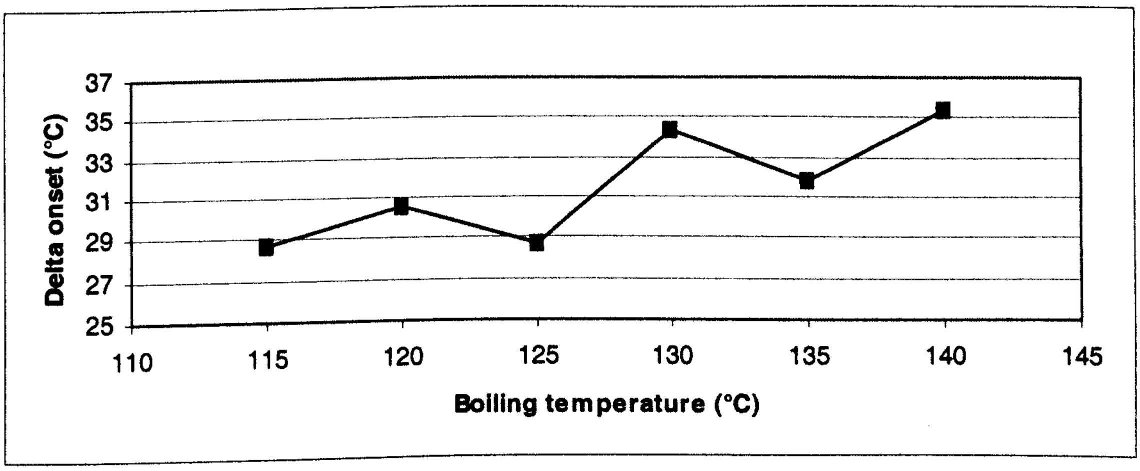

Figure 7.21: Evolution of T2-T1 with increasing boiling temperature

7.2.3. Influence of the amount of stirring

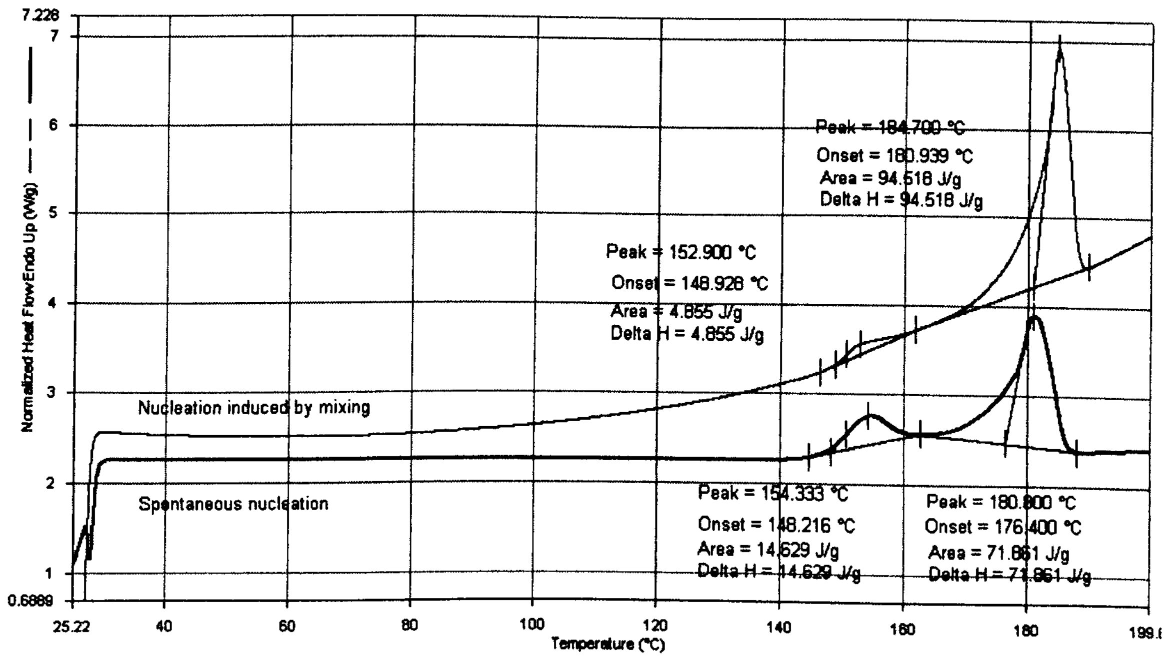

Figure 7.22: DSC traces of the low ash sucrose re-crystallised with or without stirring

The proportion of first peak was decreased by the use of the mixer (Figure 7.22). The stirring has usually the effect of speeding up the rate of nucleation[26] as well as the rate of growth.[27,28] If the phase is due to the inclusion of water in the crystal lattice, our results shows that a slow rate of nucleation and growth is needed to obtain the inclusion to trap the water. Nevertheless, it has been found that an increase in the growth rate increased the inclusion concentration.[29,30]

7.3. Isolation of the phase

The different parameters found to optimise the intensity of the peak at ca. 150°C were used to re-crystallise sucrose by evaporating a sucrose solution laid in a thin film and placed in an oven at 50°C and 70% of relative humidity (Method 9.6.2) and to obtain the phase pure by DSC analysis. Figure 7.23 shows the DSC scans and the values for the peak, onset and enthalpy of the sucrose before and after re-crystallisation using the above method. The difference between the melting points of the two phases is about 40°C. The enthalpy of the two materials is quite similar but the shape of the peak for the re-crystallised sugar is a little broader. The re-crystallised low ash sucrose (Method 9.6.2) was analysed by HPLC, the invert sugar content was similar to that of the same sucrose re-crystallised with Method 9.6.1 (i.e. 0.22%). This result indicates that the intensity of the peak at ca. 150°C is not linked to the amount of invert sugars formed during the re-crystallisation of the sucrose.

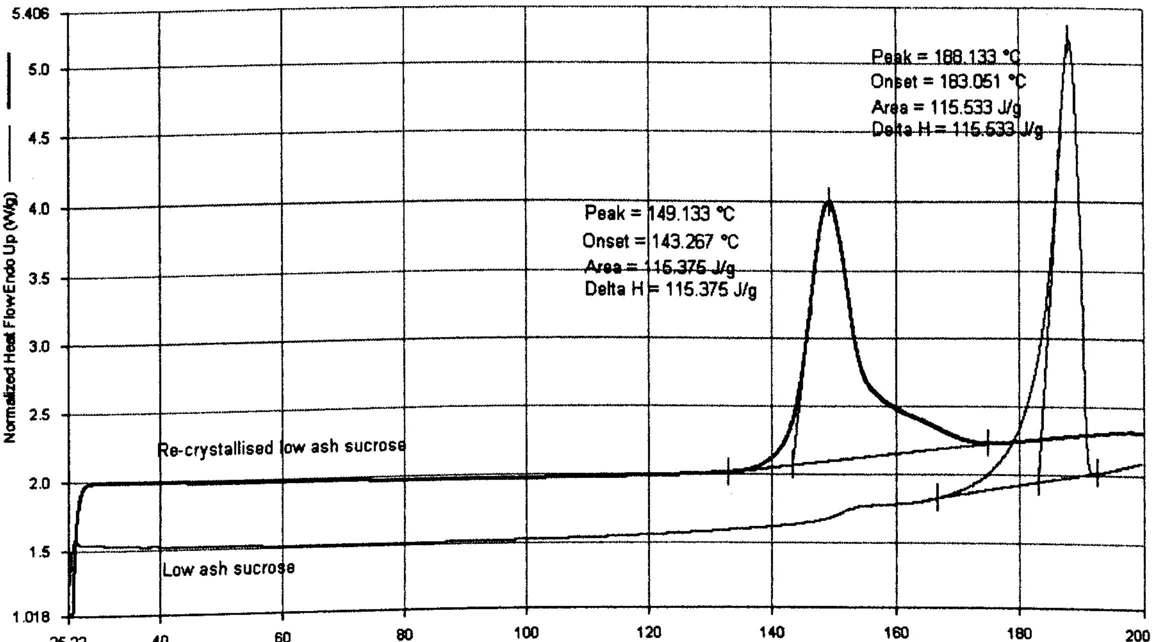

Figure 7.23: DSC traces of the low ash sucrose, commercial and re-crystallised in stagnant solution (Method 9.6.2)

Using the same method of re-crystallisation, a high ash sucrose (Lancaster) was also re-crystallised. Figure 7.24 shows the DSC trace of the re-crystallised high ash sucrose compared with the low ash sugar. Whilst the re-crystallisation Method 9.6.2 can increase the proportion of the hydrated form in the high ash case, the mineral salts inhibit the isolation of the pure hydrated form as is obtained in the low ash case.

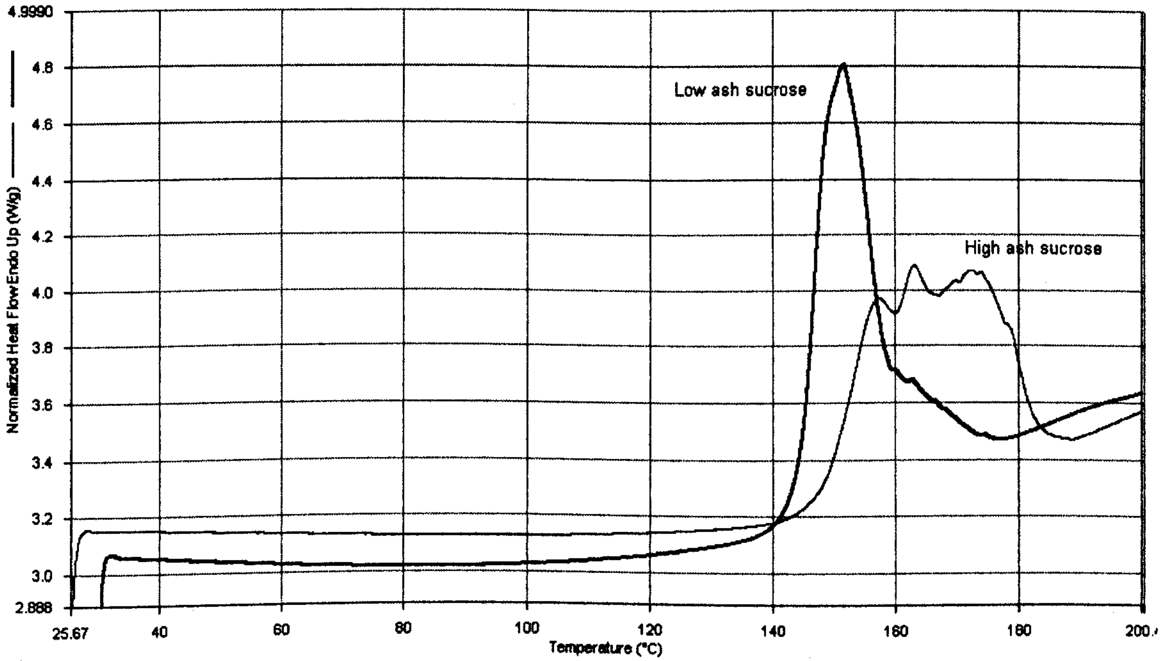

Figure 7.24: DSC traces of low ash sucrose (Fisher) and high ash sucrose (Lancaster) re-crystallised in stagnant solutions (Method 9.6.2)

Figure 7.25 shows the DSC scans of re-crystallised high ash sucrose (Tate and Lyle) using Method 9.6.2 with and without purification using an ion-exchange resin. The isolation of the hydrated form can be observed in the purified sugars.

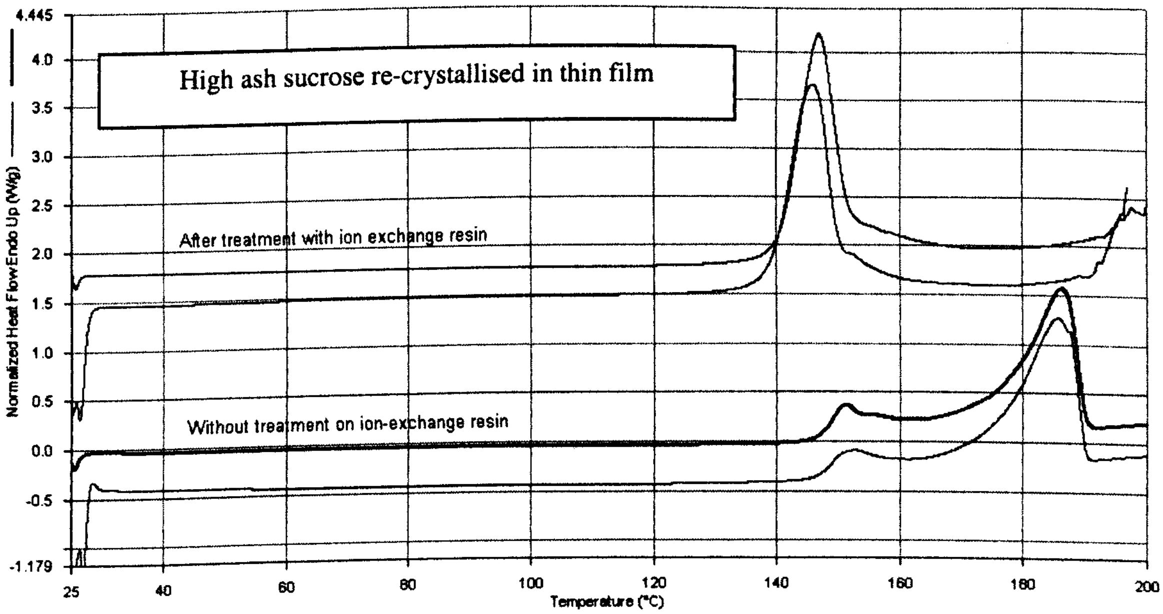

Figure 7.25: DSC traces of the high ash sucrose re-crystallised in stagnant solution (with or without purification on ion exchange column)

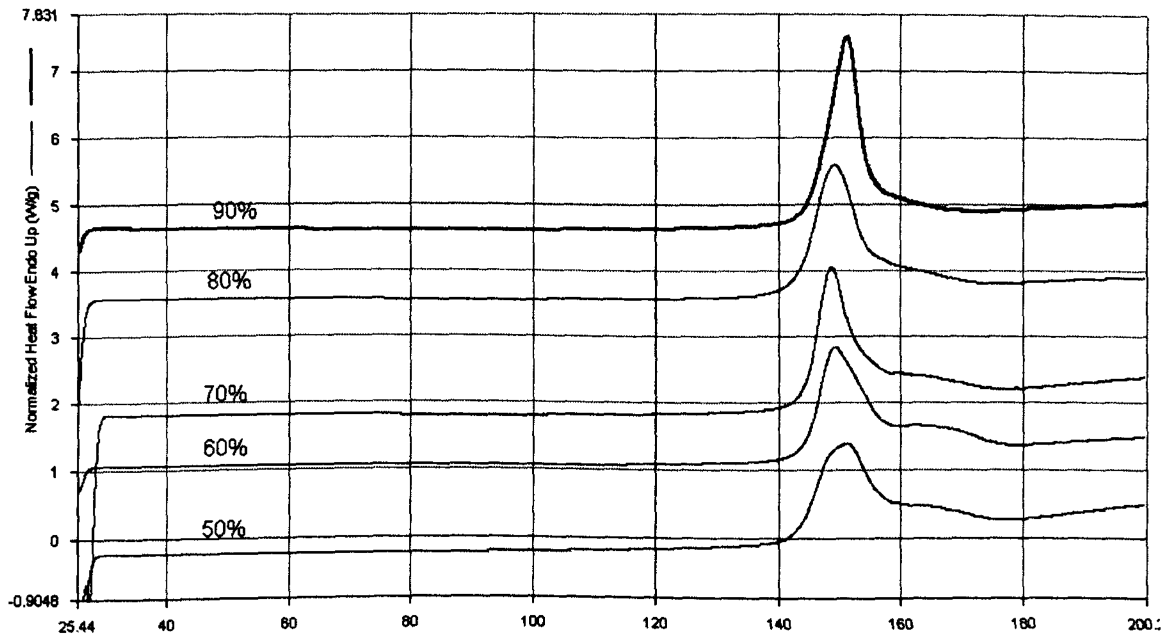

Figure 7.26: DSC traces of the low ash sucrose re-crystallised in stagnant solutions with varying relative humidity

The experiment of re-crystallisation of sucrose from a low ash sucrose (Fisher Chemicals) in thin film (Method 9.6.2) was repeated at the different relative humidities of 40, 50, 60, 80, and 90% respectively. DSC profiles are shown in Figure 7.26.

On average, the peak tends to be better defined when the humidity in the cabinet is higher, which would confirm that water is the principal factor responsible for the observed phenomenon. In addition, the influence of the kinetic of crystallisation is important, since the nucleation rate was observed to be much slower at higher humidities.

7.4. Characterisation of the phase

Confirmation of the transition peak at ca. 150°C, as determined by DSC analysis was confirmed by Hot Stage Microscopy (HSM) which gave an onset at 145.9°C, and by transparency observation which gave a melting point of 154.2°C. Figure 7.27 shows the evolution of transparency with increasing temperature. When compared to the melting of commercial sucrose, the increase of transparency was much slower for the hydrated sucrose. The same observation was made visually by HSM.

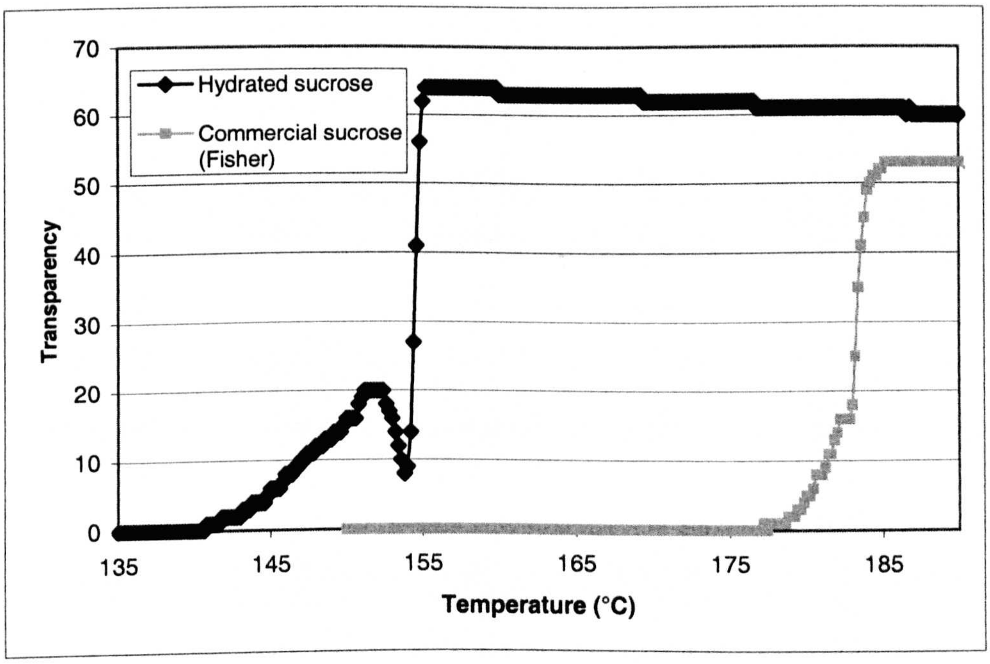

Figure 7.27: Evolution of the transparency with increasing temperature of commercial low ash sucrose and the same sugar re-crystallised in thin film

Thermogravimetry analysis was used to measure the loss of weight during heating and determine at which temperature such a loss might occur. Thus, crystals were heated from room temperature to 200°C. A loss less than 1% was observed throughout the whole range of heating. The low weight loss reflects the low amount of water in the crystals which was confirmed by moisture content measurements determined by Karl Fischer analysis which gave an average of 0.7 ± 0.25% of water in the crystals.

No obvious difference between commercial sucrose and the hydrated form was detected by Infra Red analysis and X-ray powder diffraction (Figure 7.28). Furthermore, measurement of the refractive index of the material by the Becke line method indicated that it was in the range of normal sucrose.

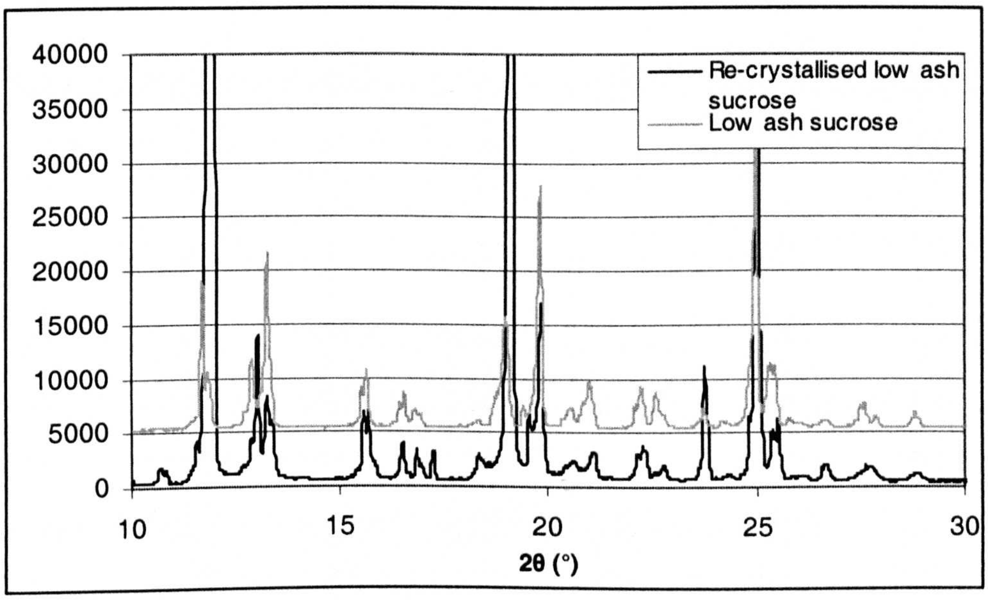

Figure 7.28: X-ray diffraction pattern of a commercial low ash sucrose and the same sugar re-crystallised in thin film

These analyses were not consistent with a stoichiometric sucrose hydrate or the possibility of polymorphism. Thus, it is proposed that the crystalline form isolated involves a non-stoichiometric inclusion of water. When this occurs the presence of water can usually be detected by DSC. This is normally achieved by freezing the sample and then heating it.[31] The melting of ice can then be observed. This experiment was performed but no trace of the melting of ice could be detected. Such a lack of detection could be due to the low amount of water present in the material. The presence of water in the crystal could explain the slow melting of the phase. As the temperature rises, the water slowly dissolves the crystalline sucrose surrounding it, giving a much longer time to pass from the solid to the liquid state. In order to evaluate the stability of the phase, a sample of the product was further dried over P_2O_5 at 70°C during 24 h in a drying pistol. The DSC profile (Figure 7.29) shows the evolution of a higher melting phase after drying.

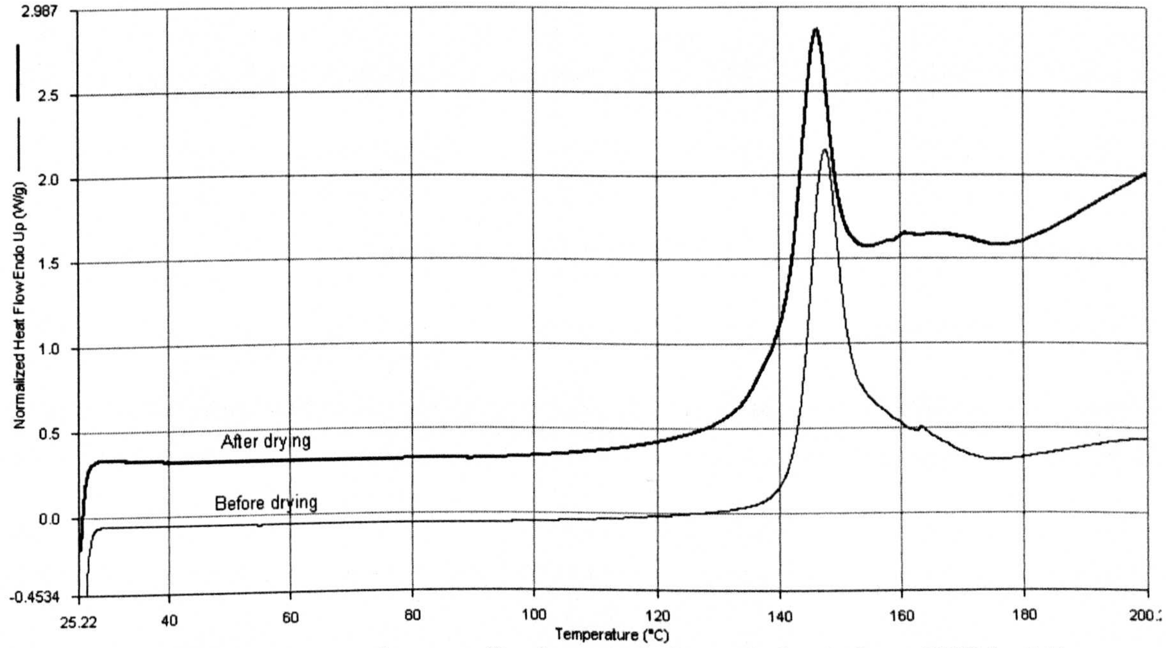

Figure 7.29: DSC traces of re-crystallised sucrose before and after drying at 70°C for 24 h

A sample of the same material was dried for 2 h at 100°C using a drying pistol. Under these conditions, the product obtained showed some signs of decomposition of sucrose. HPLC analysis of the dried product gave a content of invert sugars of 20.5%. Figure 7.30 shows the DSC scan of the material. A glass transition was observed at around 54°C. This low transition temperature compared to the literature values can be explained by the presence of the invert sugars from the decomposition. The enthalpy of the peak was only half its original value. The phase is then not stable at so high a temperature contrary to the usual form of sucrose.

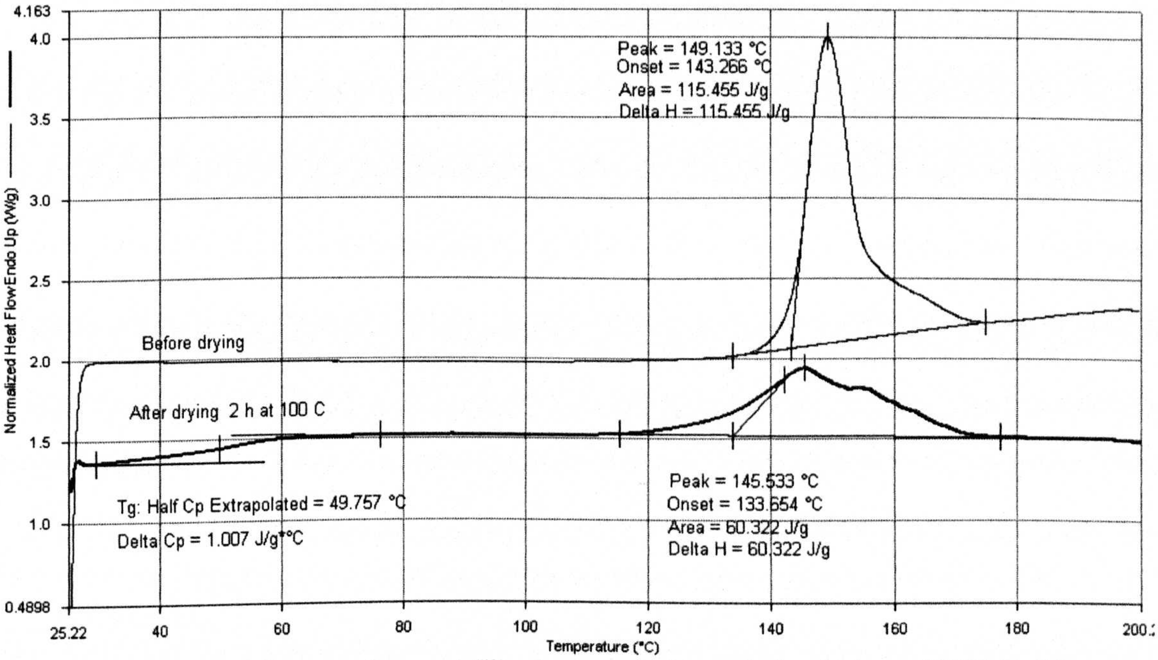

Figure 7.30: DSC traces of re-crystalllised sucrose before and after drying at 100°C for 2 h

Figure 7.31 shows the decrease in crystallinity when the re-crystallised sucrose is maintained at 110°C with increasing time.

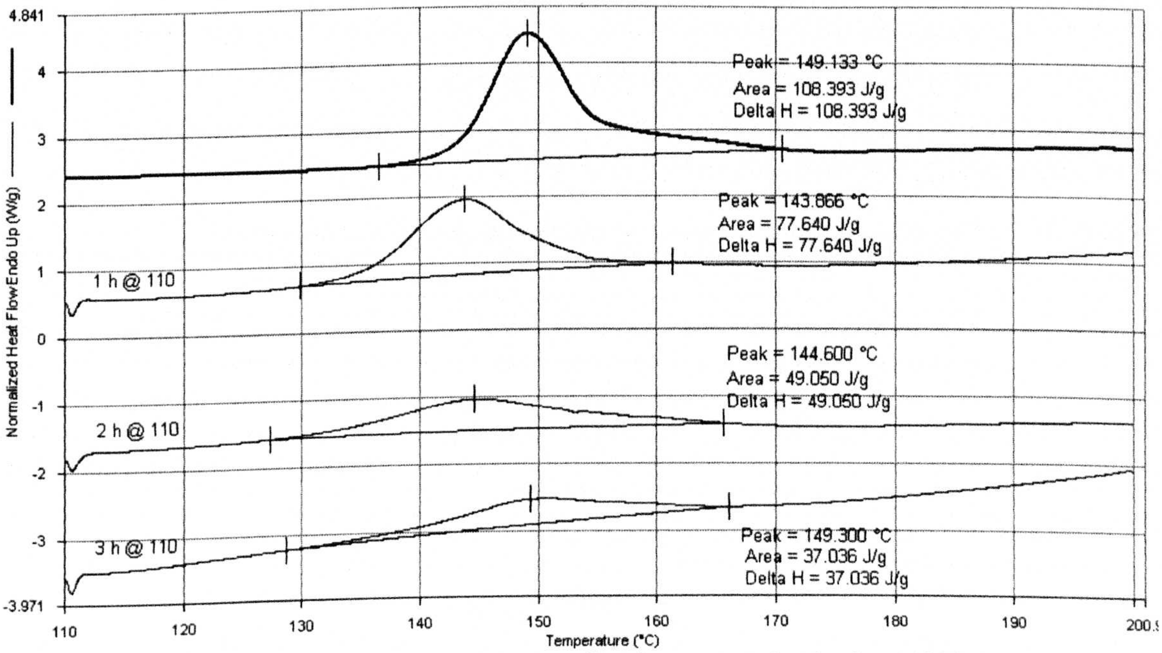

Figure 7.31: DSC traces of re-crystallised sucrose maintained at 110°C

The different analyses carried out on the phase suggest that it is caused by the non-stoichiometric entrapment of mother liquor. Early studies proposed that liquid inclusions were due to periods of subsaturation during the growth of the crystals.[32] Nevertheless, it was argued that for such a mechanism a random type of inclusion might be expected.[33] Efficiency of movement between the crystals and surrounding fluid would appear to reduce liquid inclusion by this mechanism.[34] In our case, the consistent melting point of the form of sucrose isolated would point to a more uniform pattern of inclusion but the influence of the amount of stirring is in agreement with this type of mechanism.

7.5. Conclusion

A new form of sucrose has been observed. The appearance of the phase has been found to rely significantly on the purity of the material used, especially in terms of mineral salts content, which would explained that it has been only recently reported. The impurities decrease the presence of the phase with increase interaction with water. The level of supersaturation, rate of nucleation have been shown to affect the intensity of the phase. Isolation of the phase has allowed us to further characterise the material. Its water content analysis, melting profile and X-ray powder diffraction pattern bring us to the conclusion that this transition is due to a non-stoichiometric entrapment of water in the crystal lattice.

7.6. References

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CHAPTER VIII

APPLICATIONS OF CO-CRYSTALLINE PRODUCTS IN CONFECTIONERY

8.1. Aim

The co-crystalline sucrose-glucose system has been studied on a small scale in order to determine the conditions to produce a material suitable for use in confectionery (Chapter 6). There are various examples of the use of sucrose-glucose mixtures in the food industry. Glucose can be used as a replacement for sucrose in panning[1]. Patents disclose the use of such mixtures in syrup form[2], as a coating for breakfast cereals[3,4] and fillers in chocolate[5]. Glucose has some advantages over sucrose as a food ingredient. It has a healthier image.[6] Indeed, studies have indicated that sucrose appears to be the most cariogenic sugar.[7] Furthermore, under the new chocolate regulation glucose is permitted at all levels.[8] Nevertheless, we have seen that there are drawbacks associated with the use of glucose in confectionery, especially the high boiling point temperatures of its solutions.[9] In addition, replacement of sucrose by glucose in chocolate gives a very viscous product, not suitable for the latter stages of chocolate manufacture.[10] The co-crystallisation process was thought to be a way of incorporating glucose in confectionery products without the problems associated with glucose itself. Furthermore, improved properties of a co-crystalline material over a dry blend of sucrose and glucose might be expected. For instance, a co-crystalline product has generally good tabletting properties.[11] Therefore, it was the intention to investigate the co-crystallisation of sucrose with glucose in more detail than previously reported (Chapter 6) and make comparison between small and large scale procedures. An important aim was to investigate the co-crystalline materials for their: capacity to retain flavours; effect on the viscosity of chocolate; effect on fat migration and relate these properties to the physical characteristics of the material prepared in order to understand their mechanism of action in such applications with view to design improved materials.

8.2. Co-crystallisation of sucrose-glucose on a larger scale

8.2.1. Sucrose as the main ingredient

A systematic approach was planned which compared co-crystalline mixtures with high and low levels of sucrose relative to glucose.

8.2.1.1 Preparation of co-crystalline products

The preparation of a co-crystalline material containing 10% of glucose was carried out under a variety of conditions to optimise on efficiency. The method described in Chapter 9 (Method 9.3.2.1) was found to be the most efficient. The use of a high shear mixer was found to be especially crucial. Previous attempts with lower shear rates failed to afford a material with a good texture and flowability. The temperature profile of the high shear material during the process is shown in Figure 8.1.

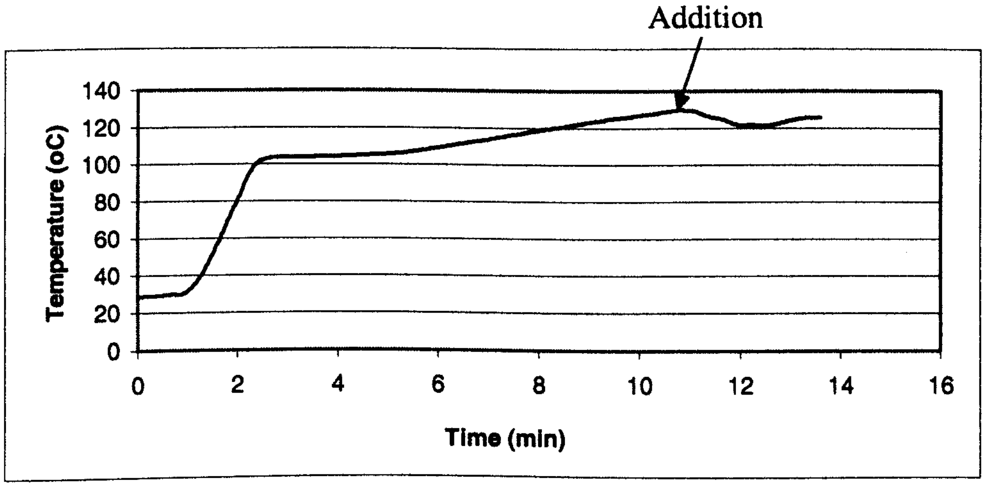


Figure 8.1: Temperature profile of the high shear mixture during the co-crystallisation process

Prior to the solution boiling, the rate of heating of the sucrose solution was about 58°C/min. Once the solution boiled, the rate was reduced to 4°C/min. Upon reaching 130°C, the addition of the glucose powder led to a drop in the temperature of the mixture. The combined effects of the energy introduced by shearing and crystallisation led to an overall increase of temperature from 122 to about 126°C.

Figure 8.2 shows the effect of varying the amount of glucose monohydrate added to the sucrose solution. It can be seen that an increase in the amount of glucose monohydrate resulted in a larger drop of the temperature over a period of 200 sec. It was observed that crystallisation was slower when a larger amount of glucose monohydrate was added. At 11% of glucose monohydrate, the mixture passed through a stage where its viscosity increased as indicated by the increased loading put upon the high shear mixer.

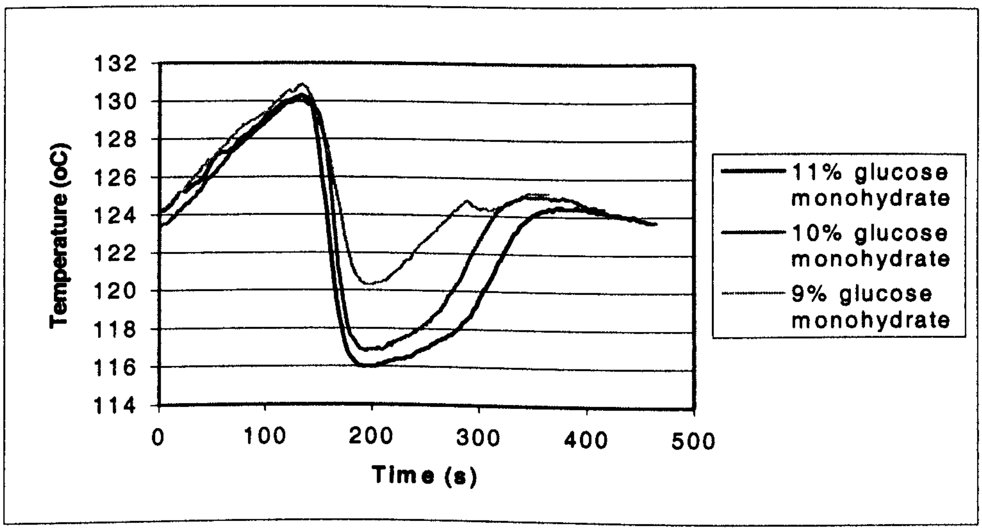


Figure 8.2: Effect of the amount of glucose monohydrate added on the temperature profile during co-crystallisation of sucrose and glucose

Figure 8.3 shows the effect of the timing of the addition of anhydrous glucose. The addition of seeds before the addition of glucose monohydrate stimulated crystallisation. The heat of crystallisation compensated for the heat lost by the addition of glucose. The temperature of the mixture was found not to drop below the temperature at which crystallisation took place (124.2°C). In contrast, the rate of crystallisation appeared to be slower in the remaining three experiments. The time at which crystallisation took place was significantly delayed when the seeds were added after the addition of glucose monohydrate. In this case, the seeds had an effect contrary to what was expected.

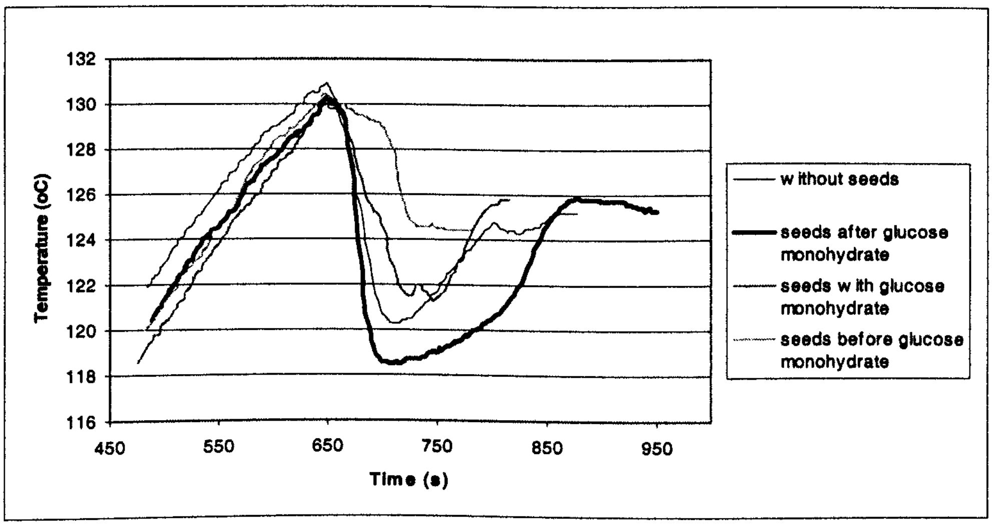


Figure 8.3: Effect of anhydrous glucose seeds on the temperature profile during co-crystallisation of sucrose and glucose

Each of the co-crystalline products prepared by Method 9.3.2.1 was consistent in having a yellowish colour presumably due to the browning reaction. HPLC analysis showed no substance other than glucose and sucrose to be present, except for a trace amount of fructose originating from sucrose inversion.

8.2.1.2. Moisture content analysis

The determination of the moisture content of co-crystalline products is important since the water content of a sugar product and the way this water is bound to the material is significant in relation to the texture and the shelf life of the final food product in which it is incorporated.[12]

Typical results obtained by Karl Fischer Analysis gave a moisture content of about 5.5% before drying and about 1.5% after drying at 45°C overnight. The percentage of water present dropped to 0.8% when the product was dried at the same temperature for 48 h. Different methods of drying were tried using a traditional oven, vacuum oven and microwave. The traditional oven gave the best drying capacity but to the detriment of the colour of the product. In the vacuum oven, the product kept its original coloration but the rate of drying was much slower. In the microwave experiments, the moisture content remained high and the product rapidly melted. A moisture content of about 0.8% was reached after drying for 3 hours at 80°C in a traditional oven. When lower water contents were reached the product showed a trend to pick up moisture and equilibrate at about 0.8%. Water activity measurements were made on the product at different moisture contents (Table 8.1).

Product	Moisture Content (%)	Water Activity	Temperature of measurement (°C)
Sucrose	0.3	0.293	21.4
Glucose monohydrate	9.4	0.331	21.5
Anhydrous glucose	0.6	0.298	21.0
Co-crystalline sucrose-glucose product	0.7	0.224	20.3
	0.8	0.256	21.4
	1.0	0.259	21.0
	1.5	0.339	20.5
	5.1	0.741	20.3

Table 8.1: Moisture content and water activity of the co-crystalline products and the raw materials used

Below a moisture content of 1% the co-crystalline material showed a water activity lower than sucrose. It can be then considered that below that level the remaining water is closely bound to the crystals.

8.2.1.3. Analysis of the solid state

An important feature of this work is to attempt to find a relationship between physical characteristics of the co-crystalline materials and their influence on the properties of a final food product.

The DSC traces of each product gave a single peak at 179°C, ΔH ~ 90 J/g (Figure 8.4). This result was reproducible. It was found that a glass transition was observed when crystallisation was slow. In contrast, no glass transition due to amorphous sugars was found on the DSC scans when crystal formation took place rapidly. Interestingly, no melting points for glucose either for the monohydrate or anhydrous forms were observed on the curves. The observation that glucose stayed in the amorphous form was confirmed by X-ray powder diffraction analysis which showed only the pattern for sucrose (Figure 8.5). Usually, the presence of anhydrous glucose in the crystalline form can be observed by a peak for 2θ at 21°.

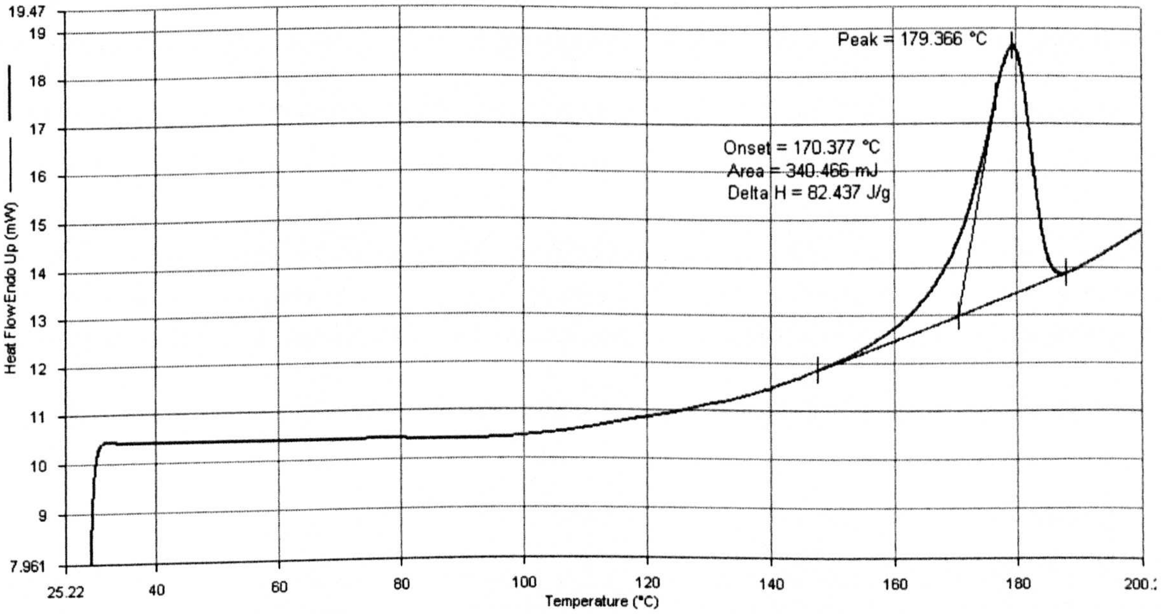


Figure 8.4: Differential Scanning Calorimetry trace of a co-crystalline sucrose-glucose product at an application scale containing 10% of glucose

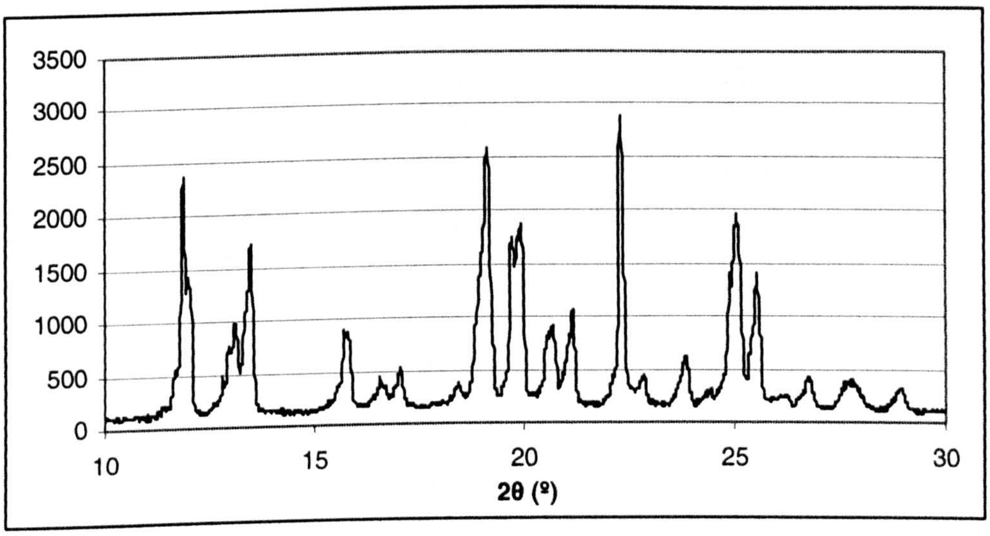


Figure 8.5: X-ray diffraction pattern of a co-crystalline sucrose-glucose product at an application scale containing 10% of glucose

8.2.1.4. Rate of dissolution

A potential advantage of co-crystalline materials is their ability to dissolve rapidly.[13] Such a property can be advantageous in a number of food applications such as instant drinks. Hence, the rate of dissolution of the co-crystalline product was determined and compared to that of a dry blend of the same materials. The first method tried, consisted of following the turbidity of a solution in which the powders were dissolved. Unexpectedly, the solution containing the co-crystalline material appeared to take a longer time to become clear (Figure 8.6). This result was surprising since the co-crystalline materials have been shown to dissolve more quickly than the dry blends.[13] It was latter found that the turbidity of the solution containing the co-crystalline material was not due to solid particles obstructing the light beam, but instead to air bubbles released from the porous co-crystalline material.

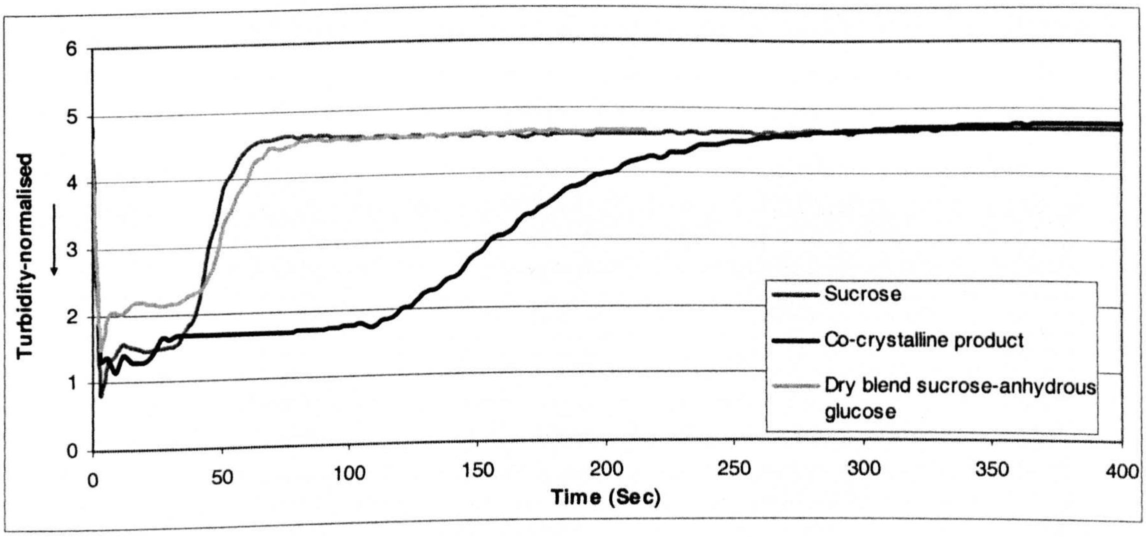


Figure 8.6: Evolution of the turbidity of a solution during dissolution of the sugars

To avoid the problems associated with bubble formation, an alternative means was sought to study the rate of dissolution. This involved following the conductivity of the solution during dissolution of the powders (Method 9.7.9). The slope of the increase in conductivity was sharper with the co-crystalline material than for sucrose or the dry blend of sucrose and glucose containing the same proportions of the sugars, showing that the co-crystalline material dissolves more quickly in water than the other powders investigated (Figure 8.7).

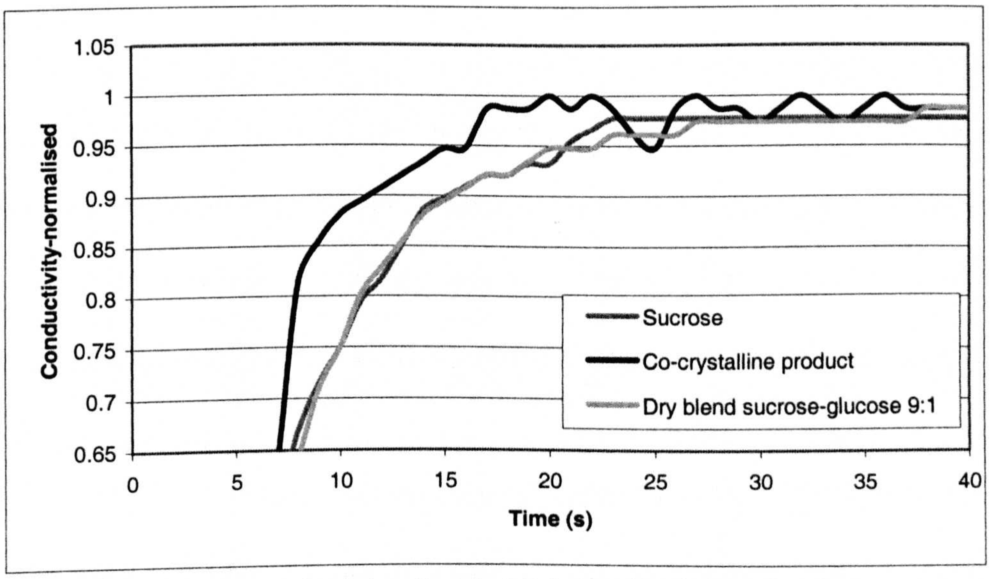


Figure 8.7: Evolution of the conductivity of a solution during dissolution of sucrose, a co-crystalline product and a dry blend of sucrose with glucose

An indication of the porosity of the co-crystalline material can be observed in Figure 8.8 which represents a photomicrograph of a co-crystalline material. The size of the sugar crystals is evenly ranged from 3 to 20 μm.

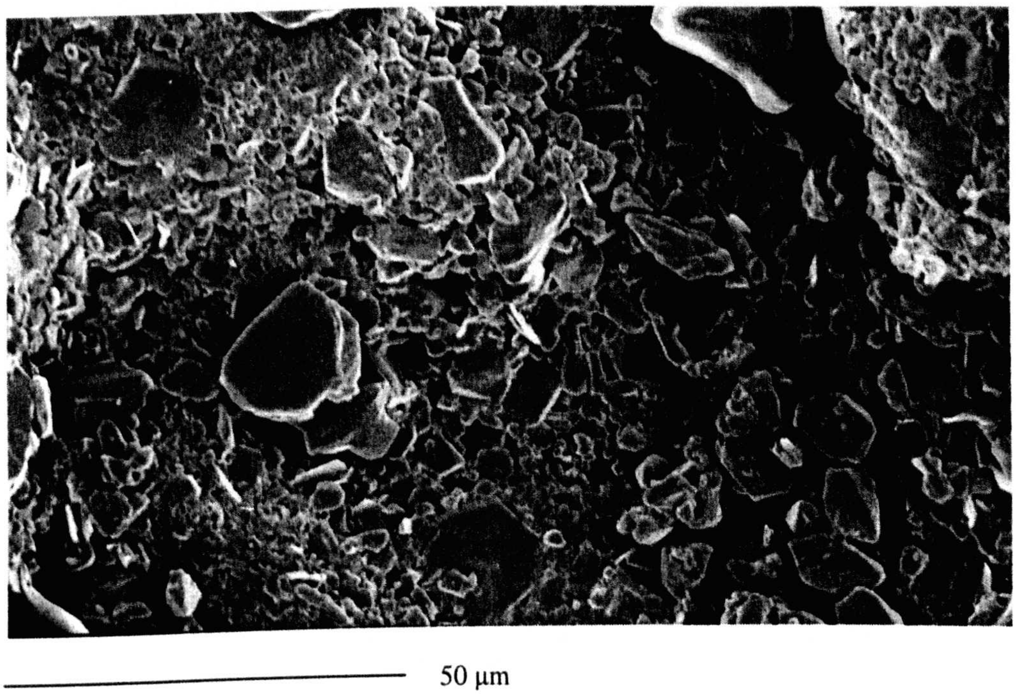


Figure 8.8: Photomicrograph of a co-crystalline sucrose-glucose product containing 10% of glucose

8.2.1.5. Incorporation of magnesium stearate

Magnesium stearate is a surfactant which is used in the food industry to improve the flowability of solids. It is especially used for the tabletting of powders as a lubricant.[14] Therefore, the incorporation of the flow agent into a co-crystalline material was investigated in order to obtain a material directly compressible. A co-crystalline product was thus prepared with magnesium stearate incorporated during the co-crystallisation step (Method 9.3.2.3). The experiment was repeated twice. Each time, the addition of the magnesium stearate seemed to accelerate the crystallisation of sucrose and it was found difficult to homogenise the mixture. The DSC analysis showed that glucose was present in a crystalline form (peak 139.133°C, ΔH = 1.530 J/g; peak 185.100°C, ΔH = 87.858 J/g). The addition of magnesium stearate thus changed the thermal profile of the product. The angle of repose of the material obtained was measured and compared to that of a similar co-crystalline product without magnesium stearate (Method 9.3.2.1) and of a dry blend of the co-crystalline product and magnesium stereate in the same proportions (Table 8.2).

Material	Angle of repose (°)	Standard deviation
Co-crystalline product sucrose-glucose-magnesium stearate (89:10:1)	37.5	0.5
Co-crystalline product sucrose-glucose (9:1)	40.0	1
Dry blend co-crystalline product sucrose-glucose (9:1) + 1% of magnesium stearate	38.5	1

Table 8.2: Angle of repose of co-crystalline products with and without magnesium stearate

The material with magnesium stearate incorporated during the co-crystallisation process showed a lower angle of repose (indicating improved flowability) than the same product without flowing agent and that the dry blend of the co-crystalline product and magnesium stearate. This might be explained by a better coating of the sugar particles by the lubricant when it is added at an early stage.

8.2.2. Glucose as the main ingredient

The co-crystalline material containing a majority of glucose was particularly intended to be tested for its tabletting properties. Indeed, there are some problems associated with the compacting of glucose. In its anhydrous form, it is not directly compressible,[15] whereas in the monohydrate form it can be compressed directly but may show signs of browning at the surface of the tablet. The only change to the method of preparation of the co-crystalline product from small to larger scale was the increase in the proportion of seeds added, i.e., from 1 to 5% (% by weight of dry matter) (Method 9.3.2).

8.2.2.1. Moisture content

As for the co-crystalline material containing a low amount of glucose, the materials prepared on an application (or large) scale were analysed for their water content and water activity. The results are shown in Table 8.3 and compared with those obtained with a similar product prepared at a small scale and containing the same proportions of the sugars (Method 9.3.1.3.3).

Material	Moisture content (%)		Water Activity	T(°C)
	Before drying	After drying		
Co-crystalline product sucrose-glucose (1:9) application scale	5.6	1.3	0.257	21.9
Co-crystalline product sucrose-glucose (1:9) application scale	–	0.9	0.257	22.0
Co-crystalline product sucrose-glucose (1:9) laboratory scale	–	1.0	0.617	21.0

Table 8.3: Moisture content and water activity of co-crystalline products containing 90% of glucose

Although the moisture content was similar between the products prepared on a laboratory and on an application scale there were differences in the water activity. The water (around 1%) was found to be more tightly bound in the case of the application scale. Indeed, above 0.5 of water activity, the water can be considered as "free". For the application scale experiments, the materials gave a water activity below 0.3 which indicates that the water cannot be released with ease. An explication to these differences could be the manner in which the sugars are crystallised in the materials.

8.2.2.2. Analysis of the solid state

The DSC scans are shown in Figure 8.9. Each product shows peaks at 144.6°C and 150.53°C which correspond, respectively, to α- and β-D-glucose. A shoulder at 156°C is present after the second peak which was at first assigned to the melting of crystalline sucrose.

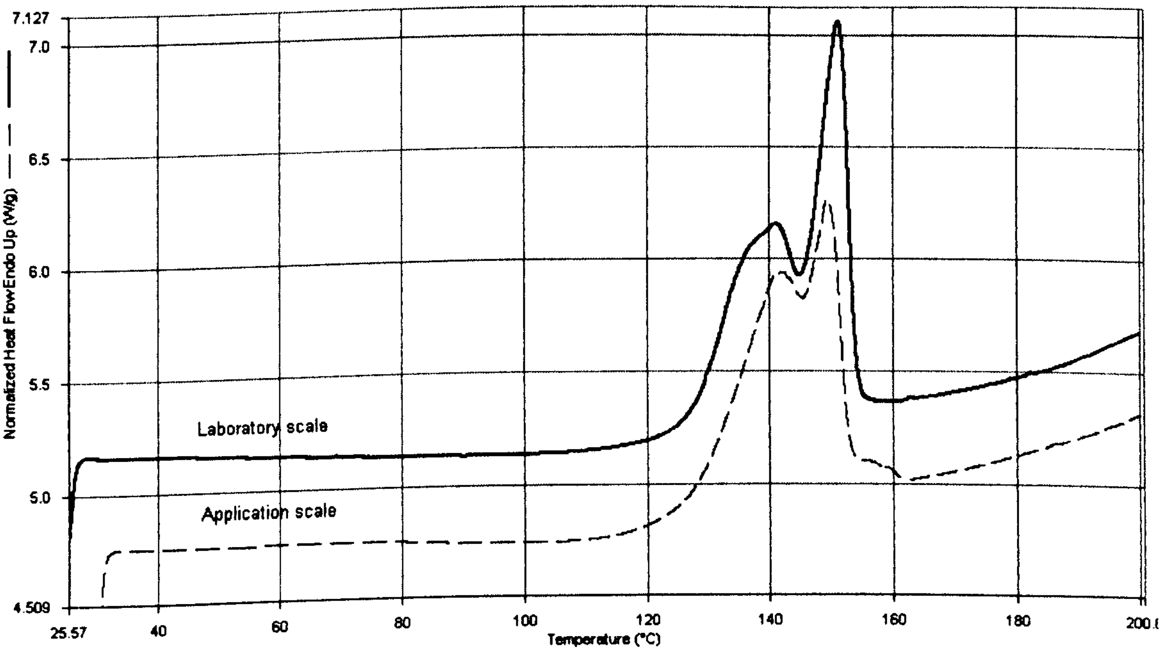


Figure 8.9: DSC traces of co-crystalline sucrose and glucose products containing 90% of glucose (laboratory scale and application scale)

In contrast to the co-crystalline product containing a large amount of sucrose, the DSC traces of the products prepared on a large scale and on a laboratory scale are very similar and the crystallisation of the sugars did not seem to be influenced by the scaling up process.

When analysed by powder X-ray diffraction, both the products prepared in the laboratory and on a larger scale showed the patterns of α- and β-D-glucose (Figure 8.10). Unexpectedly, crystalline sucrose was not present in the trace of the material prepared on a larger scale. It is usually detected by two small peaks around 2θ equal to 13°. The shoulder at 156°C on the DSC traces has yet to be explained.

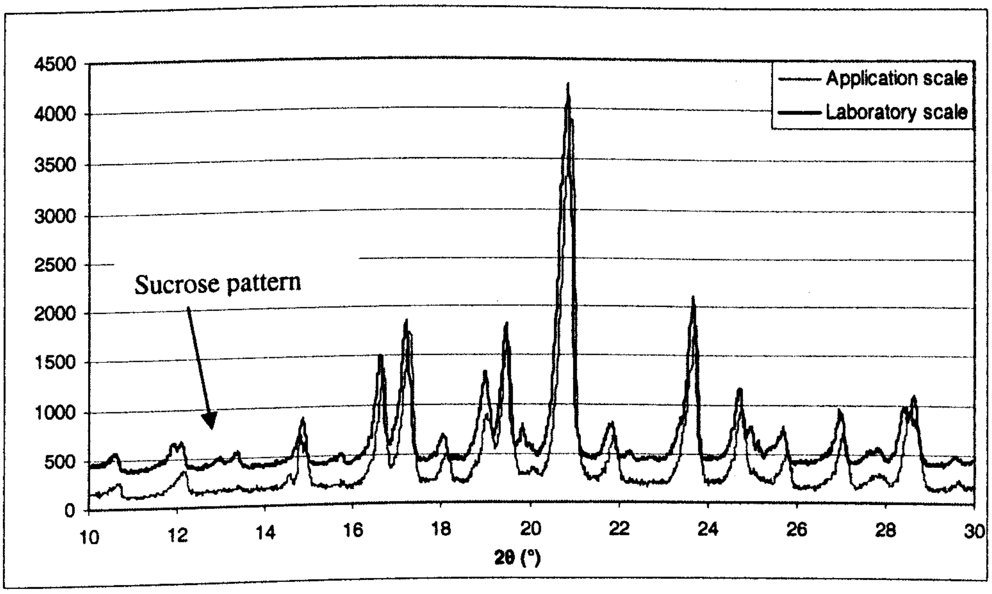


Figure 8.10: X-ray diffraction pattern of a co-crystalline sucrose-glucose product containing 90% of glucose (laboratory and application scale)

It was found that in all the large scale experiments, both when either sucrose or glucose was the major component, the minor compound in the co-crystalline product stayed in an amorphous form. Even after several months of storage, the second ingredient was found not to crystallise in the co-crystalline material. It is obvious that the cooling rate of a laboratory scale experiments is much faster. As a consequence, some of the crystals of the second ingredient might have not been dissolved when added to the sucrose solution or the molten glucose, thus such crystal may act as seeds for the remaining material. On the large scale however, the mixture stays longer at higher temperatures, allowing the second ingredient to dissolve totally in the major sugar component. With no seeds available and being homogeneously incorporated in the matrix of the other sugar, the second ingredient remains in the amorphous state.

8.2.2.3. Rate of dissolution

The rate of dissolution of the co-crystalline material containing 90% of glucose was studied by measuring the conductivity of a solution. Four different materials were tested:

- Sucrose
- Anhydrous glucose
- Co-crystalline material (Method 9.3.2.1)
- Dry blend of sucrose-anhydrous glucose (1:9).

The evolution of the conductivity of the solution is shown in Figure 8.11. The co-crystalline material dissolved more rapidly than sucrose but slower than anhydrous glucose alone or the dry blend of anhydrous glucose and sucrose. Nevertheless, in the two latter cases there were still a few particles in suspension at the end of the experiment. Even though the slope of the curve which represents the rate at which the powder dissolves is less for the co-crystalline material than for the dry blend, the co-crystalline material was fully dissolved after 2 min which was not the case for the dry blend (5 min).

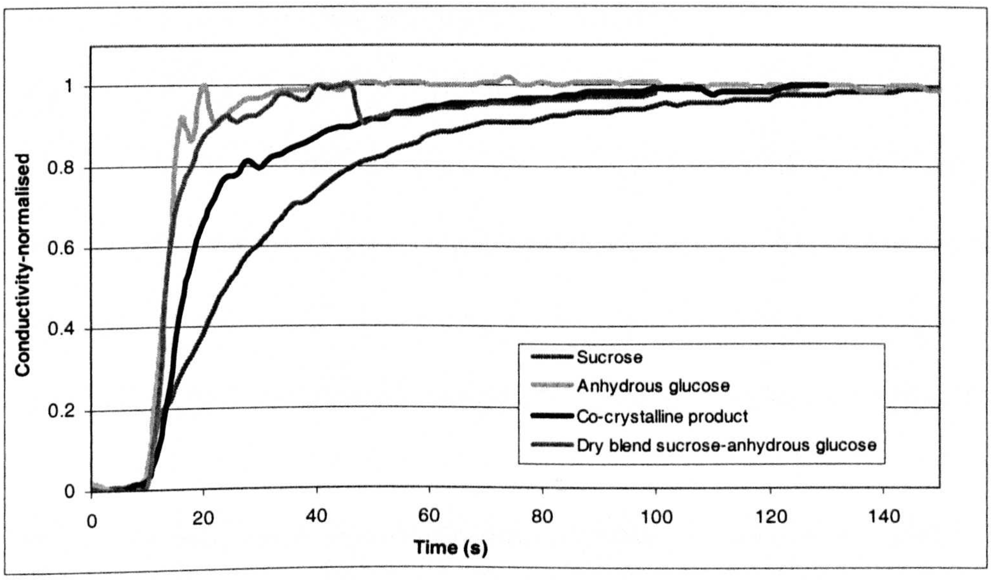


Figure 8.11: Evolution of the conductivity of a solution during dissolution of the sugars

Figure 8.12 is a photomicrograph of a co-crystalline product containing 10% of sucrose. An indication of the large surface area of the agglomerates can be observed. The size distribution of the crystals (5 - 10 μm) is more homogeneous than for the materials containing a majority of sucrose (3 - 20 μm).

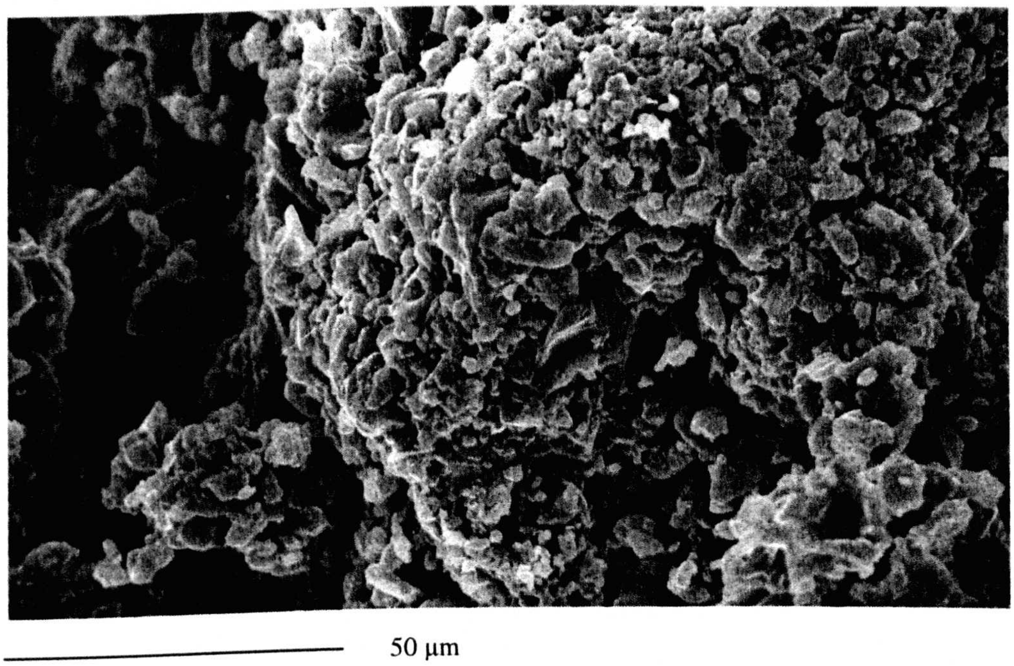


Figure 8.12: Photomicrograph of a co-crystalline sucrose-glucose product containing 10% of sucrose

8.3. Application of co-crystalline products in tabletting

Sucrose is available in directly compressible forms.[14] Nevertheless, they are usually quite expensive. Glucose is directly compressible in the monohydrate form but may show some signs of browning.[15] The co-crystalline materials: one containing a majority of glucose and the other a majority of sucrose were tested for their tabletting properties.

8.3.1. Effect of the moisture content of the co-crystalline products on the tablets strength

The moisture content of a powder influences its cohesiveness and its tabletting properties.[16] The influence of the moisture content of the co-crystalline products on the crushing strength of the tablets made from them was investigated.

The particle size distribution of a powder is one of the factors influencing the properties of the final tablets obtained by compaction.[17] The results for the particles analysis (Method 9.9.1) of the different powders used for the compressibility study are shown in Table 8.4.

Particle size of materials	Percentage of material by weight			
	Co-crystalline product 10% of glucose	Co-crystalline product 90% of glucose	Sucrose-Glucose (90/10)	Sucrose-Glucose (10/90)
> 500 μm	47.1	50.6	42.4	6.0
> 355 μm	11.1	45.1	30.2	33.0
> 125 μm	26.3	4.3	25.3	59.1
<125 μm	15.5	0.0	2.1	1.9

Table 8.4: Particle size analysis of the powders used for the compressibility tests

The dry blend containing 90% of glucose contains more fine particles than the other powders investigated. A material with more fine particles will give harder tablets when the same conditions of pressing are used since there is more material incorporated in the die (which is filled volumetrically) giving a thicker and heavier compact. The co-crystalline material containing 90% of glucose has very few particles below 355 μm which could be a drawback to giving a compact with good homogeneity.[14]

Materials	Moisture content (%)	
	Just after pressing	15 days after pressing
Co-crystalline product at 90% of glucose	1.5	1.2
Co-crystalline product at 90% of glucose dried 1 hour	1.0	1.0
Co-crystalline product at 90% of glucose dried 2 hours	0.6	1.0
Co-crystalline product at 10% of glucose	1.8	1.3
Co-crystalline product at 10% of glucose dried 1 hour	0.9	1.0
Co-crystalline product at 10% of glucose dried 2 hours	0.6	1.3

Table 8.5: Moisture content of the powders one day and 15 days after pressing

The moisture content of the compacts is shown in Table 8.5. By using different times of drying, powders with different moisture contents were obtained for the pressing.

The eight mixtures were pressed using the same conditions (Method 9.9.2). At the end of the process the co-crystalline product containing 90% of glucose that had been dried for 2 h at 60°C showed some signs of capping. The dry mixtures of sucrose and anhydrous glucose showed the same problem but to a greater extent.

The weight, thickness and hardness were each measured with the same apparatus (Method 9.9.2). Each value presented in Table 8.6 is the mean, based on assaying 10 sweets. It was not possible to perform the measurements on the dry mixture containing 90% of anhydrous glucose, as all the tablets produced were too fragile (all were laminated). This result is probably due to the large proportion of anhydrous glucose which has not adequate binding properties and cannot be compressed directly.[15]

Material	Weight (mg)	Crushing strength (N)	Thickness (mm)
Commercial tablet	1462.8 (43.9)	86 (11)	5.10 (0.08)
Sucrose-glucose (90/10)	1841.7 (12.7)	28 (5)	6.31 (0.14)
	1840.5 (15.3)	38 (7)	6.19 (0.12)
Co-crystalline product at 10% of glucose	1607.4 (28.8)	109 (10)	5.22 (0.10)
	1613.6 (39.7)	101 (4)	5.28 (0.11)
Co-crystalline product at 10% of glucose dried 1 hour	1539.0 (57.7)	82 (8)	5.22 (0.10)
	1556.5 (31.7)	106 (8)	5.27 (0.07)
Co-crystalline product at 10% of glucose dried 2 hours	1501.2 (20.3)	72 (5)	5.16 (0.05)
	1509.5 (12.7)	86 (5)	5.18 (0.03)
Co-crystalline product at 90% of glucose	1564.7 (56.7)	84 (13)	5.45 (0.09)
	1544.2 (55.7)	93 (15)	5.37 (0.13)
Co-crystalline product at 90% of glucose dried 1 hour	1533.7 (74.9)	66 (12)	5.39 (0.16)
	1578.5 (35.9)	72 (12)	5.51 (0.08)
Co-crystalline product at 90% of glucose dried 2 hours	1537.6 (31.5)	59 (6)	5.43 (0.09)
	1534.3 (17.2)	67 (11)	5.43 (0.13)

–: Results obtained just after pressing of the tablets

–: Results obtained 15 days after pressing of the tablets

Table 8.6: Crushing strength, weight and thickness of the tablets. The standard deviation is in brackets

In both cases, the co-crystalline products containing 90% and 10% of glucose, gave powders which had good tabletting properties such that their crushing strengths were similar to that of commercial Polos and much higher than the dry blends. The hardness of the tablets increased with increase in their moisture content. This result is in accordance with the work of Chen *et al.* who found that Di-Pac® (a co-crystalline material containing 3% of maltodextrins) compressed better at high moisture contents.[11] In addition, it has also been reported that an increase in the moisture content of anhydrous glucose produced a corresponding increase in the strength parameter.[18]

After 15 days, the sweets of almost all the batches prepared gained in strength with the exception of those made with the co-crystalline product containing 10% of glucose that had a high moisture content. Ahlneck *et al.*[19] have found that the strength of sucrose tablets increased after storage. They believed it to be due to a rearrangement of solid matter within the tablet. After storage for 15 days, the moisture content of all the sweets equilibrates to approximately the same level. However, the differences in hardness remained the same as was initially found. Thus, the loss or gain of water during storage had little effect on the strength of the tablet compared to the initial moisture content of the powders.

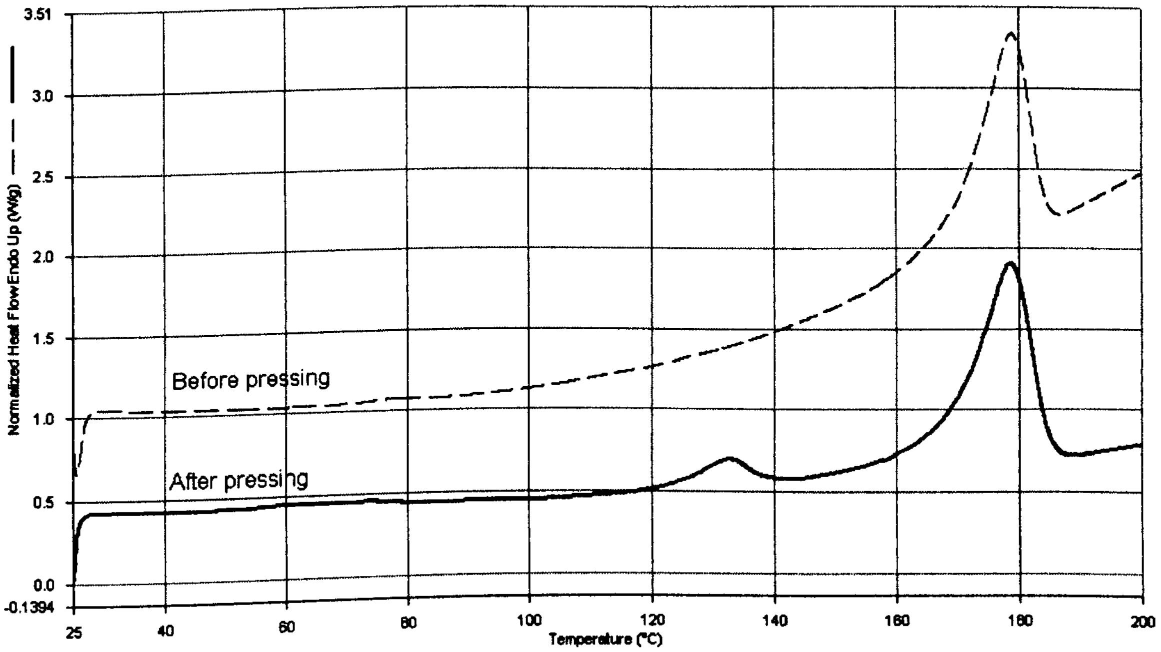


Figure 8.13: Evolution of the DSC trace of a co-crystalline product containing 10% of glucose after tabletting

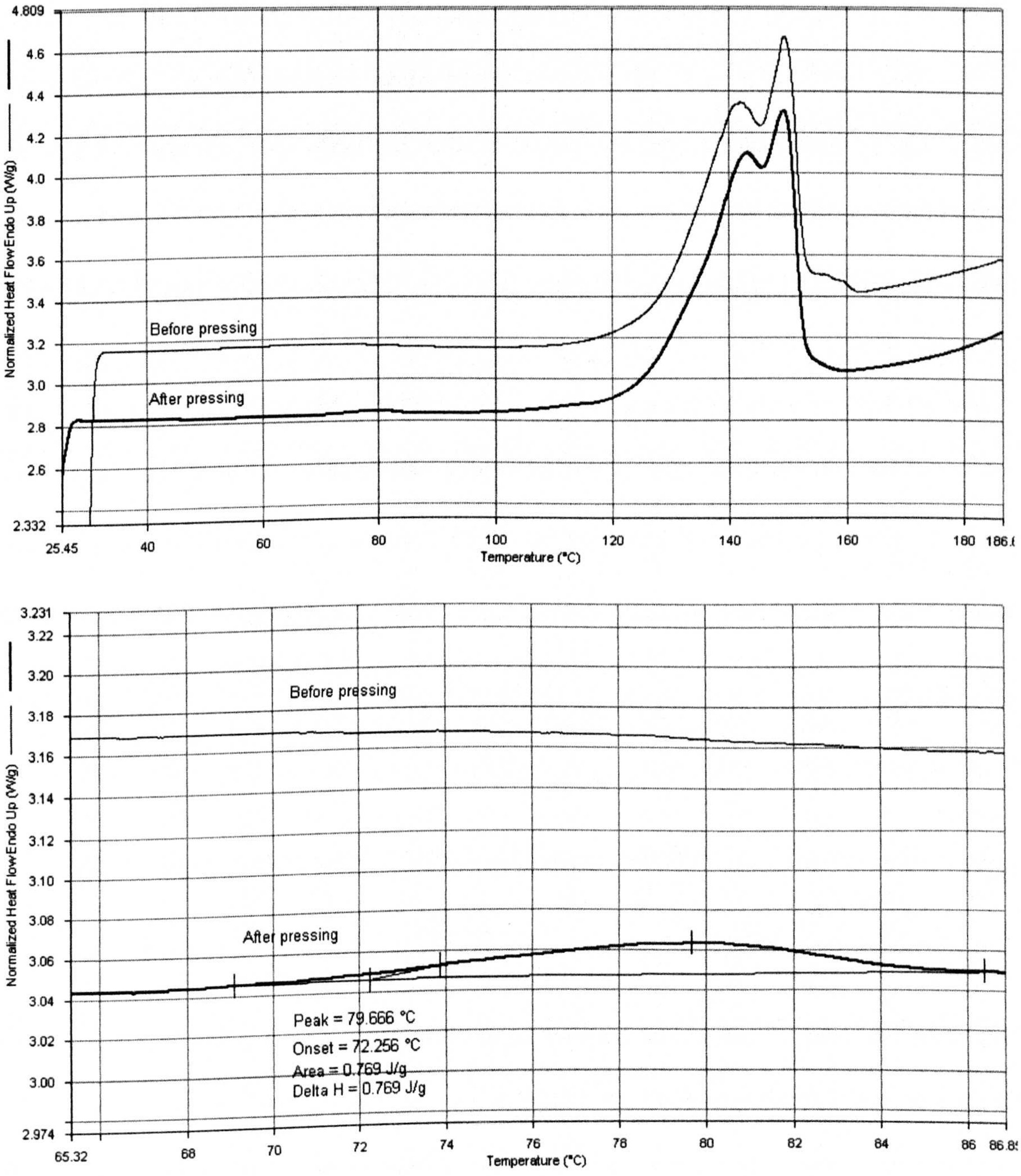


Figure 8.14: Evolution of the DSC trace of a co-crystalline product containing 90% of glucose after tabletting

The morphology of the components which relates to the type of texture of the two co-crystalline products (containing a majority of sucrose or glucose) was studied by DSC over time after pressing. In the case of the co-crystalline material containing a majority of glucose a peak appeared in some cases at around 80°C, which was assigned to glucose monohydrate in the crystalline form (Figure 8.14). Furthermore, the shoulder following the melting peaks for anhydrous glucose was found to disappear (Figure 8.14).

In the case of the co-crystalline products containing a majority of sucrose, the traces generated by thermal analysis were found to vary. In some cases, the presence of amorphous material was observed and in others the crystalline forms of anhydrous glucose and monohydrate appeared whereas they were not visible in the product before tabletting. In both cases, it could be concluded that during the tabletting step, the amorphous phase present in the products or formed during pressing passed the glass transition. In some cases this rubbery phase crystallised depending on factors which influence the point at which the sugar becomes saturated in the sweets. The crystallisation of amorphous matter could explain the good crushing strength values found for the co-crystalline materials. The crystallisation of sucrose after compression had already been observed by other researchers.[20] Re-crystallisation of glucose during tabletting may also be so extensive as to create interparticulate bridges.[21]

8.3.2. Effect of the co-crystalline products on flavour retention

Co-crystalline materials are used to encapsulate flavours.[22] Hence, the co-crystalline materials were pressed, this time with mint flavour added to the powder, and their capacity to retain the flavouring agent investigated by following the relative amount of flavour remaining during storage (Method 9.9.3). The particle size of the powder is an important factor in obtaining tablets with similar weight and thickness when using the same pressing conditions. Table 8.7 shows the particle size distribution obtained by sieving (Method 9.9.1) of the different powders tested. The co-crystalline materials containing 10% and 90% of glucose have more fine particles than in the previous experiment. The increase in the amount of fine particles would be expected to be reflected in the crushing strength of the tablets.

Material	Particle size of materials (% by weight)			
	>500 μm	> 355 μm	> 125 μm	< 125 μm
Candy Pac®	69.1	13.4	15.6	1.9
Polo granules	56.1	6.1	20.0	17.8
Co-crystalline material containing 10% of glucose	39.4	16.9	22.9	20.8
Co-crystalline material containing 90% of glucose	41.0	55.0	3.6	0.4
Co-crystalline material containing 10% of glucose and 1% of magnesium stearate	31.0	10.6	22.8	35.6

Table 8.7: Particles size analysis of the powders used for the fading of flavour experiments

Once more, the powder containing a majority of glucose was shown to possess more particles between 355 and 500 μm but with almost no particles passing through a 125 μm mesh. The commercial co-crystalline product (Candy Pac®) had a particle size distribution similar to the unflavoured granules (Polo granules) but with fewer fine particles.

Concerning the moisture content (Table 8.8), the co-crystalline product with magnesium stearate incorporated into the sucrose matrix was not dry enough with a water content of 1.9% compared to the other powders. This higher moisture content would be expected to influence the hardness of the final sweet and its capacity to retain flavour. Indeed, it has been shown[23] that a smaller amount of flavour was lost when the water content of the carbohydrate (sucrose/maltodextrin) was decreased from 3.5 to 3.1%. However, in the reported work the sugar matrix was amorphous.

Material	Moisture content (%)
Co-crystalline material containing 10% of glucose	0.9
Co-crystalline material containing 90% of glucose	0.8
Co-crystalline material containing 10% of glucose and 1% of magnesium stearate	1.9
Candy Pac®	0.7

Table 8.8: Moisture content of the powders used for the fading of flavour experiments

In this study, the strength, weight and dimensions of the sweets were measured one day after pressing (Table 8.9). The commercial co-crystalline product (Candy Pac®) gave the lowest hardness value but showed no sign of capping or lamination. Furthermore, it gave tablets with similar weight, size and hardness to tablets made from the granulated powder (Polo granules).

Material	Weight (mg)	Hardness (N)	Thickness (mm)	Diameter (mm)
Polo granules	1481.8 (15.0)	75 (3)	5.09 (0.02)	19.16 (0.04)
Co-crystalline material containing 90% of glucose	1622.5 (33.3)	79 (7)	5.55 (0.08)	19.19 (0.02)
Candy Pac®	1487.4 (14.8)	69 (5)	5.11 (0.02)	19.19 (0.03)
Co-crystalline material containing 10% of glucose and 1% of magnesium stearate	1586.0 (60.0)	80 (5)	5.31 (0.14)	19.15 (0.02)
Co-crystalline material containing 10% of glucose	1597.0 (20.7)	108 (10)	5.21 (0.05)	19.16 (0.01)

Table 8.9: Crushing strength and dimensions of the tablets containing mint oil. The standard deviation is in brackets

The co-crystalline materials prepared (Methods 9.3.2.1, 9.3.2.3, 9.3.2.4) gave heavier and thicker sweets than those made from the commercial co-crystalline product (Candy Pac®) and the granulated powder (Polo granules) due to their particle size distribution. The co-crystalline material containing 10% of glucose gave the higher values of hardness though the sweets made from it were chewy when they were freshly made.

The co-crystalline material in which the magnesium stearate had been included during the co-crystallisation process gave tablets with good hardness values though lower than when the same product was used in which the flowing agent was added afterwards. Anti-caking agents even though they improve the flowability of a powder have been found to reduce its compressibility.[24] The sensitivity of inulin tablets to the addition of magnesium stearate has been observed.[25] In our case, the co-crystalline material was found to be more lubricant sensitive when the magnesium stearate is incorporated during the co-crystallisation process. It was postulated[26,27] that the lubricant sensitivity of a material is principally determined by what happens with the magnesium stearate coating of the particles during the early stages of the consolidation process. The fact that the magnesium stearate has been added during the co-crystallisation process was thought to have improved the homogeneity of the mixture and thus the coating of the sugar particles with magnesium stearate. In contrast, in the dry blend of co-crystalline material and magnesium stearate, it is believed that the fracture of the agglomerates of the co-crystalline material during compression led to isolated patches of magnesium stearate rather than a continuous network. Consequently, there is less effect of magnesium stearate on the tablet strength.

A trace of the mint flavour obtained by gas chromatography is shown in Appendix 2. Five components of the mint flavour were chosen and the area of their peak on the Gas Chromatography trace was recorded. Menthol was not kept since its amount is too high to give reliable results on the fading of flavour. The five compounds were chosen among the more volatile molecules (lower retention times on the GC column).

Retention Time (min)	Compound	Area of the peak (pA.s)				
		Candy Pac®	Polo granules	Co-cryst. material 10% G	Co-cryst. material 90% G	Co-cryst. material 10% G + 1% mag.
17.551	Octan-3-ol	11.21 (1.15)	9.76 (1.08)	11.48 (1.36)	12.20 (1.03)	12.67 (0.96)
25.739	Menthone	607.19 (87.52)	410.96 (51.16)	858.43 (94.25)	726.98 (43.55)	921.58 (91.93)
25.852	Menthofuran	8.16 (0.33)	4.52 (0.39)	7.71 (0.79)	7.22 (0.69)	8.08 (0.50)
26.169	Menthone	258.23 (28.73)	170.17 (17.04)	311.66 (32.21)	295.46 (9.58)	337.27 (30.85)
26.329	Isomenthol	183.54 (10.27)	82.05 (5.61)	175.09 (18.93)	169.52 (13.35)	194.74 (10.71)
	Total	**1068.33 (128.00)**	**677.46 (75.28)**	**1364.37 (225.75)**	**1211.38 (68.20)**	**1474.34 (134.95)**

Table 8.10: Gas chromatography results after one week of storage. The standard deviation is in brackets

Table 8.10 shows the results of the gas chromatography analysis of the compacts after one week of storage. The co-crystalline materials gave higher values than the usual granulated powder. This is true for each of the five flavour compounds contained in the mint flavour chosen. Furthermore, this good result was observed in spite of the fact that part of the material pass through a transition from the glassy to the crystalline state which have been shown to result in a loss of volatiles.[28,29] The co-crystalline material in which magnesium stearate had been incorporated during the co-crystallisation process gave the overall highest value.

	Area of the peak (pA.s)				
Compound	Candy Pac®	Polo granules	Co-cryst. material 10% G	Co-cryst. material 90% G	Co-cryst. material 10% G + 1% mag.
Octan-3-ol	–	–	–	–	5.14 (2.33)
Menthone	95.67 (17.85)	33.19 (7.57)	37.44 (5.39)	94.80 (38.97)	867.22 90.75
Menthofuran	–	–	–	–	–
Menthone	28.13 (4.63)	–	15.13 (1.89)	35.87 (12.14)	285.72 (25.28)
Isomenthol	10.79 (0.29)	14.88 (5.68)	39.69 (2.74)	47.95 (4.16)	149.29 (3.25)
Total	**133.97** **(22.77)**	**48.07** **(13.25)**	**92.26** **(10.02)**	**178.62** **(55.27)**	**1307.37** **(121.61)**

Table 8.11: Gas chromatography results after three weeks of storage. The standard deviation is in brackets.

Table 8.11 shows the area of the peaks for the five flavour components after three weeks of storage. There was no menthofuran detected in any of the tablets. The same difference in the amount of flavour between the granulated powder (Polo granules) and the co-crystalline materials was observed; all of the co-crystalline materials giving a larger amount than the reference. The co-crystalline material in which the magnesium stearate had been incorporated during the co-crystallisation process gave the highest values, with almost none of its flavour being lost during the additional two weeks of storage. This result could possibly be explained by the homogeneity of the product. Indeed, it has been found[30] that flavour retention was lower in hard candy when the flavouring was dissolved in vegetable oil which forms a biphasic system with the sugar phase. In contrast, it was reported that dissolving the flavouring in propylene glycol allowed the volatilisation to take place from the total product giving a better retention of flavour in spite of the fact that volatility of the flavours was much higher in propylene glycol than in vegetable oil. In our case, the incorporation of magnesium stearate during the co-crystallisation process allowed a more homogeneous product to be obtained which had different flowability and tabletting properties in relation to its sensitivity to magnesium stearate. The homogeneity of the product avoided compartmentalisation of the flavour and allowed a better retention of flavour.

8.4. Application of co-crystalline products in chocolate

We have seen earlier in this chapter that there is an interest in incorporating glucose in chocolate as replacement for sucrose. However, the addition of glucose is usually followed by an increase in the viscosity of the chocolate.[10] The influence of glucose as part of a co-crystalline material included in a chocolate recipe was thus tested.

8.4.1. Effect of the co-crystalline products on the viscosity of chocolate

The co-crystalline material containing 10% of glucose (Method 9.3.2.1) was used in a chocolate recipe as a replacement for sucrose and compared to normal sucrose and dry blends of sucrose and glucose. The viscosity of the chocolates obtained was determined. Foods having similar chemical composition may exhibit totally different physical properties depending on their structure. The rheology of the product is one of the properties influenced by its structure.[31] Indeed, the particle size distribution of the solid particles of a chocolate has an influence on its final viscosity.[32] In order to compare the different materials for their viscosity, the particle size distribution is required. Figure 8.15 shows the particles size distribution of the different chocolate batches after refining. One can see that the dry blend of sucrose and glucose monohydrate has a very similar distribution to that obtained for sucrose. The dry blend containing sucrose and anhydrous glucose had more particles above 30 μm than the previous batches but the co-crystalline material showed the strongest difference with a maximum of particles around 35 μm instead of 25 μm for the other powders.

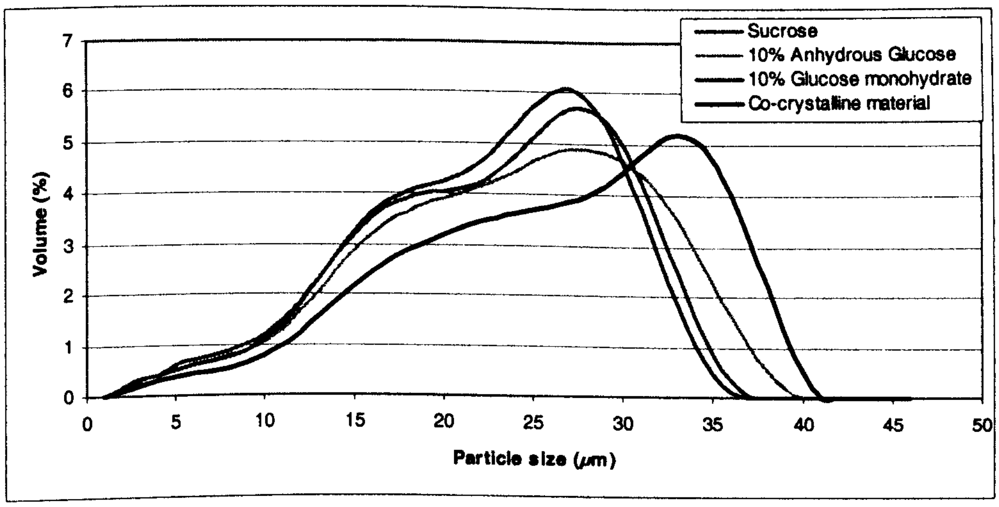


Figure 8.15: Particle size distribution of refined chocolates

Table 8.12 shows the values of D(V, 0.9) which is the size at which 90% of the particle volume is due to particles with a diameter less than this size. This value is used to characterise the particle size distribution of a chocolate. The results confirm the shape of the curve of the particle size distributions. The dry blend of sucrose and anhydrous glucose had a D(V, 0.9) around 39 μm and the co-crystalline material had a value around 55 μm.

Sugar used in chocolate	Particle size D(V, 0.9) in µm	
	Before Conching	After Conching
100% sucrose	29.09	26.80
10% anhydrous glucose	38.91	36.76
10% glucose monohydrate	26.17	25.18
Co-crystalline sucrose-glucose (10% of glucose)	55.09	55.59

Table 8.12: D(V, 0.9) of refined chocolates

The figures did not change significantly after the conching step. The target for this recipe was a D(V, 0.9) of 25 µm. All the batches had results above this value. This was due to the way the refining was carried out. Two passages in the 3-roll refiner were used to lower the particles size of the premix. Further experiments have shown that if the size of the particles was too much reduced after the first passage, it was difficult to reach the final target during the second passage through the refiner. This was particularly detrimental for the particle size distribution of the co-crystalline material. Nevertheless, refining the co-crystalline material with a target for the first passage at 100 µm permits a D(V, 0.9) as low as 20 to 25 µm to be reach after a second passage through the 3-roll refiner.

Since the co-crystalline material had more large particles than the other batches investigated it was expected that the chocolate made with it would be less viscous. Indeed, it has been reported that using a similar recipe, a chocolate made with smaller particles is more viscous.[33] However, this was not the case in our experiments with co-crystalline materials. Figure 8.16 shows the evolution of the viscosity of the chocolates with increasing shear rate. For all the batches the viscosity decreased with increasing the shear rate. Nevertheless, for a shear rate from 10 to 50 s^{-1}, the chocolate made with the co-crystalline material had the highest values of viscosity.

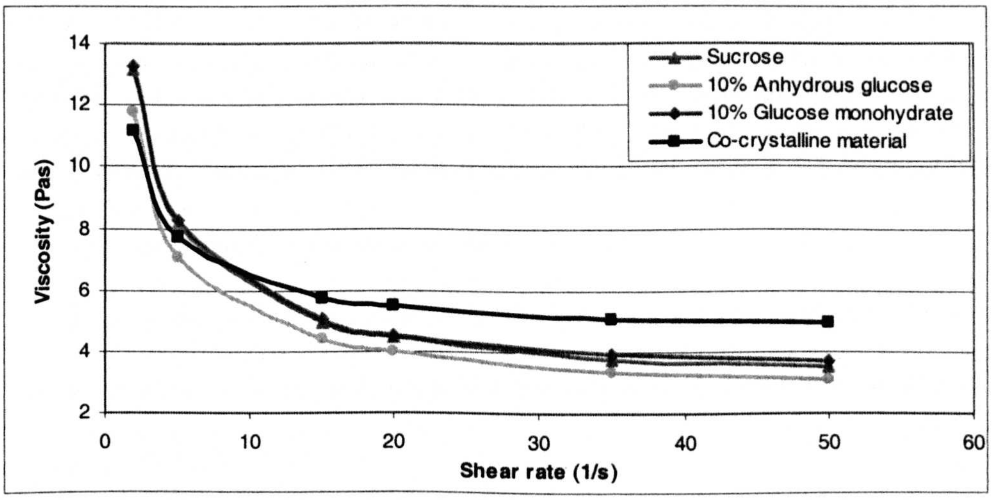


Figure 8.16: Evolution of the viscosity of the chocolates with increasing shear rate (Data from the ascending ramp)

Figure 8.17 shows the evolution of shear stress with increasing shear rate. The slope of the curves is more significant for the co-crystalline material. This slope relates to the plastic viscosity (ηp) of a material. Table 8.13 gives the values for the plastic viscosity and the yield value of the different batches of chocolate.

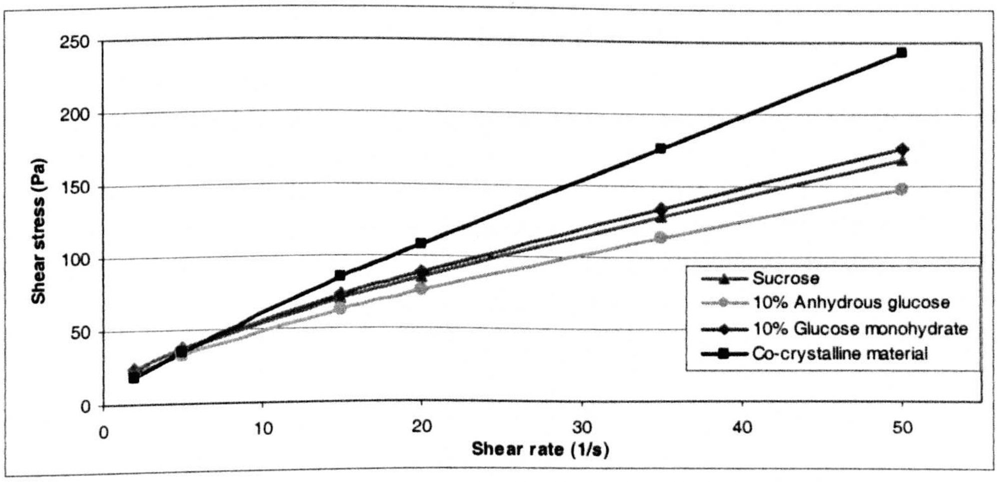


Figure 8.17: Evolution of shear stress of the chocolates with increasing shear rate (Data from the ascending ramp)

The difference of plastic viscosity between the chocolates made with the dry blends can be explained by their different particle size distribution. In contrast, the plastic viscosity obtained for the chocolate made with the co-crystalline material is in opposition with its value of D(V, 0.9). Therefore the particle size distribution cannot explain the difference of behaviour of the co-crystalline material. The use of the co-crystalline material in chocolate had also an effect on its yield value. The chocolate made with the co-crystalline material began to flow with a shear stress of only 2 Pa whereas the other chocolates studied began to flow with a shear stress of 8 Pa.

Sugar used in chocolate	Plastic viscosity η_p (Pa.s)	Yield value T (Pa)
100% sucrose	2.1	8.1
10% anhydrous glucose	1.8	7.7
10% glucose monohydrate	2.2	8.0
Co-crystalline sucrose-glucose (10% of glucose)	4.0	2.2

Table 8.13: Plastic viscosity and yield value of the chocolates

It has been reported that for a comparative chocolate recipe, when the particles are smaller, the yield value increases dramatically and the plastic viscosity also increases but less significantly.[33] According to the results from the particle size distribution, the co-crystalline material has bigger particles than the reference (100% sucrose). Therefore, the yield value would be expected to decrease. This is the case in our experiments. The plastic viscosity would also be expected to decrease, though less sharply. However, for this parameter, this is not the case in our experiments with the co-crystalline materials. The results from the particle size distribution alone cannot explain the values for the viscosity parameters. In addition, the increase in viscosity cannot be explained by the presence of glucose in the sugars which is known to thicken up chocolate. Indeed, glucose represents 10% of the sugars and this proportion did not affect the viscosity of the chocolates prepared with the dry blends of sucrose and glucose. Such a difference may be due to the moisture present in the co-crystalline material. The water at the surface of the sugar particles is known to increase the viscosity of a chocolate.[33,34]

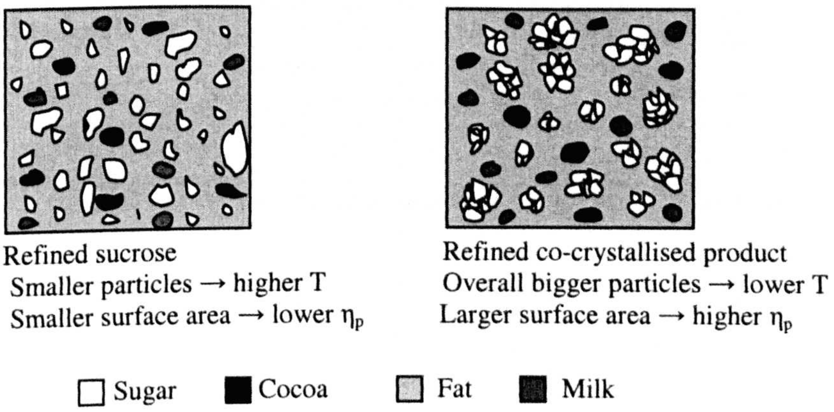
Therefore a second batch of chocolate was prepared with the same co-crystalline material dried further. The value for the moisture content was lowered significantly from 1.4 to 0.8%.

The values of the D(V, 0.9), plastic viscosity and yield value for this new batch are given in Table 8.14. The refining of the premix led to a particle size distribution closer to the target fixed. Nevertheless the reduction of the moisture content had not improved the value of the plastic viscosity. For this parameter, 9 Pa.s was achieved instead of 4 with a moisture content of 1.4% and the yield value was only of 0.2 Pa. This is in spite of the fact that extra cocoa butter and PGPR were added for this new batch (Method 9.8.1.2). PGPR is a surface agent which has an important effect on the yield value, by decreasing it sharply but it has a relatively small effect on the plastic viscosity.[33,35]

Sugar used in chocolate	Particle size D(V, 0.9) in μm		Plastic viscosity η_p (Pa.s)	Yield value T (Pa)
	Before Conching	After Conching		
Co-crystalline product (1.4% moisture content)	55.09	55.59	4.0	2.2
Co-crystalline product (0.8% moisture content)	39.93	46.79	9.0	0.2

Table 8.14: Particle size distribution and viscosity results for chocolates made with co-crystalline materials of different moisture content

In this second assay, the yield value follows a normal trend. It was found to decrease with removal of moisture and the addition of extra cocoa butter and PGPR. In contrast, the result for the plastic viscosity is contrary to what was expected. It was found to increase even though the moisture had been removed and extra cocoa butter and emulsifier had been added. It may be concluded therefore that the moisture content of the co-crystalline product is not the main reason why this product gave a very viscous chocolate. It is believed that the particular structure of the co-crystalline material is responsible for this effect on the parameters indicating the viscosity of chocolate. Indeed, the co-crystalline material is composed of agglomerates of tiny crystals of sugar. The particle size distribution gave a very high D(V, 0.9) in the case of the co-crystalline material. However the bigger particles were composed of tiny crystals agglomerated together to form a sponge like material. These agglomerates can therefore adsorb more fat that normal sucrose particles would due to an increased surface area. The removal of some of the moisture at the surface of the sugar particles has only increased the surface area available for the lipid phase to coat the agglomerates, increasing further the viscosity of the chocolate for the second batch of chocolate prepared. The yield value, on the other hand, indicates the shear stress at which a chocolate will begin to flow. For the chocolate to start flowing, the points contact between the sugar particles need to be broken[33] and these points of contact are those between the agglomerates and not between the tiny crystals of sugars. The yield value is then linked to the size of the agglomerates whereas the plastic viscosity is linked to the surface area of the sugar particles. Such a hypothesis would explain the contrary results found for the two parameters namely plastic viscosity and yield value.



Refined sucrose
Smaller particles → higher T
Smaller surface area → lower η_p

Refined co-crystallised product
Overall bigger particles → lower T
Larger surface area → higher η_p

Figure 8.18: Representation of the solid particles and fat within milk chocolates made with sucrose (left) and a co-crystalline material (right)

8.4.2. Effect of the co-crystalline products on fat migration

We have seen in the previous section (8.4.1.) that the co-crystalline product used for replacement of sucrose in chocolate seemed to adsorb more of the chocolate's lipid phase than sucrose itself. If this is the case, a co-crystalline material could be used to slow down the fat migration in coated confectionery. For this purpose, the migration of hazelnut oil from a Gianduja layer into a dark chocolate layer was studied. Indeed, hazelnut oil from fillings causes the chocolate to bloom more rapidly upon storage hence the co-crystalline products could find commercial application by suppressing this migration.[36]

Two batches of Gianduja were prepared following the recipe given in Method 9.8.2. One was prepared with sucrose, the other with a co-crystalline material containing 10% of glucose. The values of D(V, 0.9) which characterise the particle size distribution for the Gianduja made with sucrose and the co-crystalline material were very close to the target which was 20 μm (Table 8.15). Therefore both materials were sufficiently similar in character to undertake a realistic comparative trial.

Material	D(V,0.9) (μm)
Sucrose	20.24
Co-crystalline material	20.89

Table 8.15: D(V, 90) of Giandujas made with sucrose and a co-crystalline material

In order to follow the migration of the hazelnut oil in the dark chocolate layer, the proportion of triolein was determined by HPLC. The cocoa butter used in the preparation of the dark chocolate does not contain any triolein whereas it is the main component of the hazelnut oil. Appendix 3 shows HPLC traces of the starting dark chocolate, the starting Gianduja and a sample of dark chocolate in which triolein was present. Tables 8.16 and 8.17 give the retention time of the main triglycerides of the cocoa butter and the hazelnut oil respectively. The ratio of triolein to total triglycerides was thus determined in the samples to investigate the extent of migration.

Retention time (min)	Triglyceride
23.61	POP
27.83	POSt
33.00	StOSt

Table 8.16: Retention time of the main triglycerides contained in cocoa butter

Retention time (min)	Triglyceride
17.09	OOL
20.59	OOO
23.91	POP
28.20	POSt
33.45	StOSt

Table 8.17: Retention time of the main triglycerides contained in hazelnut oil

Figure 8.19 shows the evolution of the percentage of triolein in the dark chocolate layer upon storage when the Gianduja was prepared with sucrose and the co-crystalline material. Three points were taken for each measurement. The points linked by a line are the average values.

One can see that when the Gianduja was prepared with sucrose, the percentage of triolein present in the dark chocolate was consistently higher than when the Gianduja was prepared with the co-crystalline material. This is in agreement with Smith[37] who suggested that smaller non-fat solid particles reduce the migration rate by increasing the tortuosity of the diffusion path or the entrapment of liquid oil. In our case, the agglomerates of tiny sugar crystals reduced the migration rate in comparison to normal refined sucrose crystals.

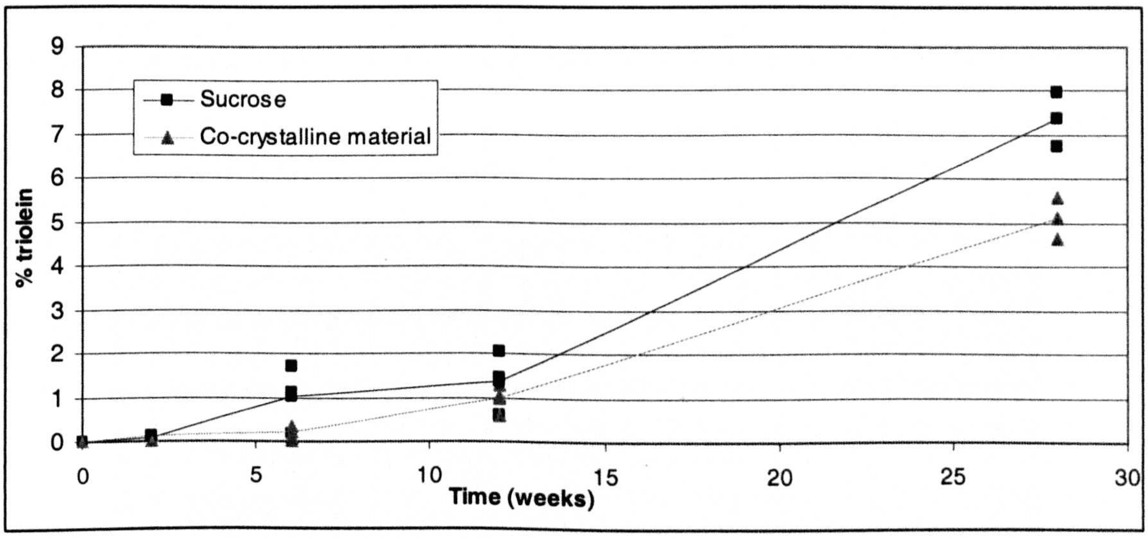


Figure 8.19: Evolution of the percentage of triolein in dark chocolate upon storage

After 6 weeks, the dark chocolate layer started to bloom in both cases. After 28 weeks of storage, in the case of the co-crystalline material, the bloom was present on the entire surface whereas for sucrose, the bloom was present on the edges and coarser (Figure 8.21). It is thought that the high percentage of triolein present at the centre of the samples prevents cocoa butter crystallisation. After 28 weeks of storage, the entire surface of the Gianduja layer prepared with sucrose was found to bloom whereas the Gianduja prepared with the co-crystalline material failed to bloom (Figure 8.20).

Figure 8.20: Gianduja surfaces after 28 weeks of storage: co-crystalline material (left) and sucrose (right)

Figure 8.21: Dark chocolate surfaces after 28 weeks of storage: co-crystalline material (left) and sucrose (right)

8.5. Conclusion

The scale up of the preparation of the sucrose-glucose co-crystalline materials has shown that even though a product containing 15-20% of a second ingredient (sucrose or glucose) can be readily prepared on a laboratory scale, it is difficult to incorporate more than 10-11% of a second ingredient with batches of 5 Kg. Furthermore, the amount of shear applied to the mixture to induce crystallisation was found to be crucial to obtaining a material with a fine texture suitable for commercial applications. Another difference observed on scaling up the process was the different crystallisation behaviour of the second ingredient. On laboratory scale experiments, the second ingredient was found at least to be partly in the crystalline form which was not the case on larger scale experiments. The incorporation of magnesium stearate in a sucrose matrix changed this result by accelerating the crystallisation of sucrose and glucose.

The use of the co-crystalline products for the preparation of tablets showed that the powders did not require the addition of any binding agent to be compressible. The crushing strength of the compacts increased with increase in the moisture content of the powder. Furthermore, the tablets slightly hardened upon storage for both low and high moisture cases. The amount of flavour remaining in the tablets prepared with the co-crystalline products was found to be higher than with the usual granules. This difference of behaviour was found to increase when the flowing agent was incorporated during the co-crystallisation process.

The use of a co-crystalline product in chocolate gave a very viscous texture to the chocolate due to the large surface area of the co-crystalline product. This property was used to test hazelnut oil migration from fillings into a dark chocolate layer. The presence of co-crystalline material significantly inhibited the bloom of the filling and decreased the migration of hazelnut oil to the covering chocolate.

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CHAPTER IX

EXPERIMENTAL

9.1. Materials

The co-crystalline materials containing honey were prepared with the following raw materials: analytical grade sucrose from Fisher Chemicals, "Australian Eucalyptus Honey" (clear honey) and "Set Honey" (granulated honey) from Tesco. Glucose monohydrate was purchased from Avocado. In its anhydrous form, the glucose used was purchased from Fisher Chemicals. Spray dried glucose syrups and maltodextrins under the trade names C☆Sperse® and C☆Dry® were obtained from Cerestar. C☆ Sperse® products have fewer fine particles than C☆Dry®. Table 9.1 shows the dextrose equivalent and composition of the various maltodextrins and glucose syrups.

Spray dried glucose syrups and maltodextrins	Dextrose Equivalent	Composition (%)			
		Dextrose	Maltose	Maltotriose	Higher saccharides
C☆Dry MD 01915®	18.5	1.0	6.0	9.0	84.0
C☆Dry GL 01924®	28.0	3.0	13.0	16.0	68.0
C☆Dry GL 01934®	38.0	1.0	33.0	23.0	43.0
C☆ Sperse MD 01318®	18.5	1.0	6.0	9.0	84.0
C☆Sperse GL 01328®	28.0	3.0	13.0	16.0	68.0
C☆Sperse GL 01338®	37.5	2.0	34.5	18.0	45.5

Table 9.1: Composition of the different spray dried glucose syrups and maltodextrins[1]

Granulated sucrose from Fisher Chemicals and high ash sugars obtained from various sources i.e. Silver Spoon, Tate & Lyle and Lancaster were used for the experiments involving the re-crystallisation of sucrose. The salts, KCl, NaCl and K_2SO_4 and the Amberlite monobed ion exchange resin MB-1 were purchased from BDH Ltd. The polar aprotic solvents, DMSO and DMF were acquired from Aldrich and Avocado Research Chemicals Ltd respectively. The sugars used for the applications experiments (larger scale) were anhydrous glucose C2402 and glucose monohydrate C2001 from Cerestar and sucrose from British Sugar. Candy-Pac, used for the tabletting experiments, was purchased from Domino Speciality Ingredients. It is composed of 96.5% of sucrose and 3.5% of corn syrup.

9.2. Co-crystallisation sucrose-honey

Sucrose (100 g) was dissolved by mixing with water (25 g/100 g of sucrose) in a beaker and heating on a hot plate. Once the temperature of the syrup reached 128°C, the beaker was removed from the heating source. At this point a known amount of honey (room temperature) was added to obtain three different proportions of sucrose:honey (90/10, 85/15, and 80/20). The mixture was then agitated using a mixer. Within a few seconds spontaneous nucleation occurred and the product was allowed to cool to room temperature. As soon as the product was cooled, two different methods were followed. The first is similar to that previously reported[2], in which the mixture was removed from the vessel, placed onto watch glasses and dried in an oven at 40°C overnight. The second method consists in using centrifugal filtration in order to remove the excess of honey or syrup that has not been solidified. The centrifuge used was a Centaur 2, run at 3600 RPM. The product introduced into the centrifuge tubes was weighed before and after filtration. The product was then placed on watch glasses and dried. In both cases, the agglomerates obtained were ground to a powder using a mortar and a pestle and stored in screw top glass bottles. Each product was made in duplicate.

9.3. Co-crystallisation sucrose-glucose

9.3.1. Laboratory scale experiments

9.3.1.1. Sucrose as the main ingredient

Sucrose (100 g) and purified water (25 mL) were used to make a syrup which was heated to 128°C to reach a concentration of about 95% by weight of dry matter. Upon reaching this temperature the heat was removed. Almost immediately after, glucose was added in the proportions 10, 15, 20% by weight of dry matter. Glucose was incorporated in three different forms respectively: anhydrous glucose (dry method); glucose monohydrate (both at room temperature); a concentrated solution of glucose (70%) at 100°C (wet method). The mixture was stirred with a mixer to initiate nucleation of the sucrose and left to cool to room temperature. The agglomerates were filtered by centrifugation. The remaining solid was dried over phosphorus pentoxide overnight. The products were ground using a mortar and a pestle and stored in glass bottles.

9.3.1.2. Sucrose as the main ingredient with the addition of a flowing agent

A mixture of sucrose (100 g) and purified water (25 mL) were heated to 128°C. The syrup was removed from the heating source and anhydrous glucose (11.1 g) and stearic acid or magnesium stearate (1 g) were added rapidly. The resulting mixture was stirred vigorously and left to cool to room temperature to give a co-crystalline product that was dried over P_2O_5.

Alternatively, the flowing agent was added before the sucrose solution was boiled.

9.3.1.3 Glucose as the main ingredient

9.3.1.3.1. Experiments under vacuum

The method was based on that published in the patent by M.J. Daniels[3]. A solution containing glucose (99 g) and water (100 mL) was prepared. This solution was heated with an oil-bath at 125°C and concentrated under vacuum at about 125 mbar. The temperature was monitored from the oil-bath and not from the solution. The vacuum was supplied by a pump varying from 50 to 130 mbar during its application (60 min). The final concentration of the glucose solution was not accurately reproducible from one experiment to another. Once the solution was concentrated, anhydrous glucose (1 g) was added, first alone and then with three different amounts of sucrose giving a final content respectively, of 10, 15 and 20% (percentage by weight of dry matter) of sucrose. Ground sucrose was used but which was still in a crystalline form. The mixture was stirred for about 20 sec.

Once the product was cooled to room temperature, it was filtered under centrifuge to remove the syrup. Finally, the filtered product was dried in a desiccator over P_2O_5 overnight and ground to a fine powder.

The experiments were made in duplicate. A second series of samples were prepared by concentrating under vacuum for a longer period (80 min).

9.3.1.3.2. Experiments at atmospheric pressure

A solution containing glucose (99 g) and water (70 mL) was prepared. This solution was heated over a range of temperatures from 128 to 137°C. Prior to the addition of sucrose all the solutions showed a yellowish coloration due to the partial decomposition of the sugar. The initial concentration of glucose was increased to 99 g of glucose for 30 mL of water in order to diminish the heating time and thus minimise the decomposition reactions. Solutions were heated to 130, 133 and 137°C respectively (only a temperature of 137°C was used when glucose alone was added). After these temperatures were reached, the solutions were allowed to drop by 15°C. As described in 9.3.1.3.1, anhydrous glucose (1 g) was added, first alone and then with three different amounts of sucrose giving a final content of respectively, of 10, 15 and 20% of sucrose. In contrast with 9.3.1.3.1, the sucrose used was some icing sugar (icing sugar contains some amorphous form but is mainly crystalline). The mixture was stirred for about 20 sec. Once the product was cooled to room temperature, it was filtered under centrifuge. In each case no syrup was obtained by filtration. On occasions when the experiment generated a sticky paste the product was discarded. Finally, the product was dried in a desiccator over P_2O_5 overnight and ground to a powder.

9.3.1.3.3. Experiment with molten glucose monohydrate

The experiment was repeated at three different temperatures where the glucose monohydrate (108.9 g) was melted and heated to 120, 130 and 140°C respectively. In each case the flask was removed from the heating source and the temperature was allowed to drop by 10°C. Anhydrous glucose (1 g) was then added along with three different amounts of icing sugar, giving a final content of sucrose of 5, 10, and 15%.

The mixture was then vigorously stirred using a mixer. The product was set aside to cool and permit crystallisation to take place. In each case, centrifugal filtration failed to give a filtrate.

9.3.1.3.4. Sucrose as the main ingredient with addition of a flowing agent

Glucose monohydrate (108.9 g) was melted and heated to 130°C. The heating was stopped and the temperature was allowed to drop to 120°C. At this point, anhydrous glucose (1 g) was added and the mixture was vigorously stirred with a mixer. Icing sugar (11.1 g) and either stearic acid or magnesium stearate (1 g) were added and stirring of the mixture was continued. The temperature of the crystals was left to drop to room temperature. Finally the product was ground and dried over P_2O_5 overnight. An alternative protocol involved the addition of the flowing agent before the glucose monohydrate was melted.

9.3.2. Application scale experiments

9.3.2.1. Sucrose as the main ingredient

A solution of sucrose (4.5 Kg) and water (2 Kg) was prepared in an open steam-boiling pan. The mixture was heated with gentle stirring to about 130°C. The temperature was recorded with a Grant data logger. Upon reaching the temperature of 130°C, the heating was stopped and the solution was mixed using a batch Silverson high shear mixer at full speed. Almost immediately, glucose anhydrous (500 g) was added. The high shear was continued until crystallisation took place which was after about 1 min. The mixture was then poured into a bucket and spread on a table to form a layer of about 1 cm deep.

Once solidified the brittle product was broken into lumps and passed through a 2-roll granite refiner. The agglomerated crystals were then spread onto trays and stored in a hot room at 45°C overnight. Afterwards, the material was ground in a mini Stephan and sieved (1 mm mesh).

9.3.2.2. Sucrose as the main ingredient with addition of magnesium stearate.

Sucrose (4.5 kg) and water (2.25 kg) were heated to 130°C. At this point the solution was vigorously stirred using a high shear mixer and then anhydrous glucose (50 g) was added. Once the mixture was completely homogenised, glucose monohydrate (495 g) and magnesium stearate (50 g) were added and the high shear was continued until crystallisation took place. The nucleating solution was transferred in a bucket and then spread in a layer of 1 cm deep on a table. When the product had solidified and cooled, it was broken into large pieces and passed through a 2-roll refiner and then dried in an oven for two hours at 50°C.

9.3.2.3. Glucose as the main ingredient

Glucose monohydrate (4207 g, 85% by weight of the final solid content) was melted and heated to 135°C. The heating was then stopped and the temperature was allowed to drop to 125°C. At this point, anhydrous glucose (225 g, 5%) was added and the mixture was vigorously stirred using a high shear mixer. After about 2 min, icing sugar (500 g, 10%) was added. Once all the sugar was incorporated, the high shear was stopped. The mixture was then gently stirred with a spatula, transferred to a bucket and spread on a tray to form a layer of about 1 cm deep. The product was left to cool to room temperature. Once crystallised, the product was broken into large pieces and passed through a 2-roll refiner, first with a gap between the rolls of about 1 cm, then a second time with a gap of about 2 mm. Finally, the product was dried for 3 hours at 60°C. The method was repeated once.

9.4. Sucrose-glucose dry blends.[4]

A range of mixtures of icing sugar and anhydrous α-D-glucose were prepared in the ratios (by weight) (1:4, 2:3, 3:2, 4:1). The mixtures were each ground using a mortar and a pestle. The experiment was repeated using a range of mixtures of granular sucrose and α-D-glucose both from Fisher Chemicals in the ratios 1:9, 1:4, 3:7, 2:3, 1:1, 3:2, 7:3, 4:1, 9:1. Two methods of mixing were employed. The first consisted of grinding the reagents separately and then mixing them. The second involved weighing the fractions of each component and then grinding them together for 1 min. The work was repeated with a longer time of grinding (2 min).

9.5. Co-crystallisation sucrose-glucose syrups and maltodextrins

The co-crystallisation process was carried out with sucrose from Fisher Chemicals and a second ingredient of anyone of six types of glucose syrups or maltodextrins. Each was added in the proportion of 10% by weight. Centrifugation was applied to the products. In addition, the maltodextrin MD01915® and the spray dried glucose syrup GL01934® were each co-crystallised with sucrose from Silver Spoon and Fisher chemicals respectively. Each spray dry powder was added to the respective sucrose sample in the range of proportions 5, 10, 15 and 20%. The materials were each filtered by centrifugal filtration.

9.6. Sucrose re-crystallisation experiments

9.6.1. Re-crystallisation by cooling[5]

9.6.1.1. General method

A mixture of sucrose (100 g) and purified water (25 mL) was heated at different temperatures to reach different level of concentrations. Three types of high ash sucrose were used, namely those from Tate and Lyle, Lancaster and Silver Spoon. A low ash sugar from Fisher Chemicals was also used. Once the temperature was reached the solution was removed from the heating source. At this point the solution was vigorously stirred for 30 sec a spatula to initiate the crystallisation. The temperature of the solution was allowed to drop to room temperature. The crystals were dried over P_2O_5 overnight.

9.6.1.2. Experiments in presence of mineral salts

The same method as above was repeated with potassium chloride, sodium chloride and potassium sulphate respectively present in the initial solution of sucrose from Fisher Chemicals. These salts were added at different concentrations, namely 0.1, 0.5 and 1% by weight of dry matter.

9.6.1.3. Removal of mineral salts

A solution at 61.5% by weight of sucrose from Silver Spoon was prepared using purified water. This solution (100 mL) was passed through a column (diameter: 2.5 cm) packed with a monobed ion exchange resin (50 g). The exchangeable ions were H^+ and OH^-. The treated solution was re-crystallised following the method described in 9.6.1.

9.6.1.4. Successive re-crystallisations

The method described in 9.6.1.1 was followed. Then 1 hour after crystallisation, the product was filtered by centrifugal filtration at 3600 RPM for 25 min. The crystals recovered were dried and used again in method 9.6.1.1. The procedure was repeated three times.

9.6.1.5. Re-crystallisation in presence of an aprotic solvent

The method described in 9.6.1.1 was used with the difference that before applying any stirring to nucleate the solution either DMF or DMSO were added in the concentrations 2, 5 and 10% (by weight) respectively.

9.6.2. Re-crystallisation by evaporation[6]

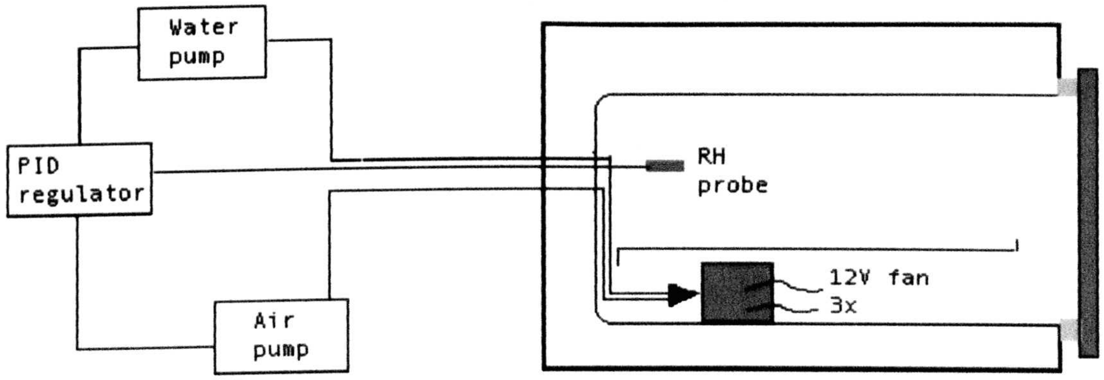

Figure 9.1: System of relative humidity control in the oven

Solutions of 61.5% concentration (solid weight/total weight) of sucrose from Fisher Chemicals in deionised water were prepared. They were warmed at 50°C for 10 min. After dissolution they were filtered through a sinter of porosity 4. The solution (25 mL) was put into a Petri dish (9 cm of diameter) which was placed in an oven at 50°C and 70% RH. The crystals obtained were washed with ethanol, crushed and dried over P_2O_5 overnight. The experiment was repeated with relative humidities of 40, 50, 60, 80, and 90% respectively. In order to maintain a constant relative humidity during all of the time of the experiment, the oven was fitted with a water and air pump controlled by a PID regulator (Figure 9.1). The relative humidity above the dishes was measured with a RH probe and recorded with a data logger. The probe was calibrated before each experiment with saturated solutions of LiCl and K_2SO_4.

9.7. Analysis techniques

9.7.1. Differential Scanning Calorimetry analysis

The endotherm scans of the different materials were obtained by Differential Scanning Calorimetry, using a scanning rate of 10°C/min from 25 to 200°C with gold as reference. A Pyris DSC 7 (Perkin Elmer) connected to a low temperature refrigerator system (Intracooler II PE) was used. Dry nitrogen was used to purge the sample head and glove box. The instrument was calibrated using indium at the same scanning rate as the samples. The product (5 mg) was weighed in sealed aluminium pans.

9.7.2. X-ray powder diffraction

Identification of the crystalline sugars present in the different samples was achieved by powder X-ray diffraction. A Bragg instrument in reflection mode with radiation of wavelength 1.54056 Å provided by a copper filter was used. The samples were scanned with 2θ ranging from 10 to 30°. Data acquisition was taken at a step size of 0.02° and a step time of 1 sec giving a scan time of 17 min 21 sec. For re-crystallised sucrose, the samples were scanned with 2θ ranging from 5 to 80°.

9.7.3. Flow property[7]

The angle of repose was used to characterise the flowability of the co-crystallised products. The agglomerates that passed through a 1000 μm but not a 500 μm mesh sieve were poured slowly through a glass funnel with an outlet diameter of 12 mm, to form a heap on a ceramic tile. The cone formed had a diameter of between 5 and 8 cm. The angle formed by the slope of the material and the base of the cone was measured 4 times for each sample using a protractor.

9.7.4. HPLC analysis of the sugars

The amount of sugars in the co-crystalline materials, were analysed by HPLC using a Gilson 203 pump and an Apex Carbohydrate column (25 cm) from Jones Chromatography. The different sugars were detected by a Sedex 50 light detector (T = 42°C) and the traces recorded using a Chessell BP 2404 recorder. The mobile phase passing through the column was acetonitrile-water (4:1) at a flow rate of 2 mL/min. Each time 20 μL of a solution containing 0.15 g of product per 50 mL of water was injected. The samples were analysed in duplicate. Calibrations curves for sucrose, fructose and glucose were constructed with the pure materials. The relations between the intensity (mV) of the peaks and the amount of sucrose, fructose and glucose in the sample were found to be respectively, $y = 6209.6x$ ($R = 0.99$, retention time: 8 min 30 sec), $y = 8164.3x$ ($R = 0.99$, retention time: 5 min 1 sec) and $y = 6866.8x$ ($R = 0.98$, retention time: 5 min 46 sec).

9.7.5. Water content and water activity[8]

The moisture content of the different materials was determined after drying using a Karl Fischer Orion Turbo 2 and a Hydranal-composite reagent. The conditions of dilution of the samples (0.5 g) were as follow:

Solvent: methanol-formamide (1:1)

Temperature of the water bath: 50°C

Turbo speed: 3

Turbo time: 5 min

Each measurement was done in duplicate. If the difference between the two measurements was above 0.25%, the two measurements were repeated.

The water activity of the co-crystalline materials was obtained by measurement of the dew point using an Aqualab Decagon CX-2 water activity meter.

9.7.6. Microscopy

The samples were sprinkled on to double sided sticky tape placed on Aluminium SEM stubs. These were placed in a dessicator for 60 min prior to sputter coating 2×4 min with gold/palladium. The coated samples were immediately examined using a Hitashi

S-1200 Scanning Electron Microscope operated at 10 kV. Three separate samples preparations of each sample were carried out on three different dates and examined separately.

9.7.7. Conductivity[9]

Conductivity measurements were carried out on solutions of sugars at a concentration of 28% by weight prepared with purified water and using a Jenway 4510 Conductivity Meter.

9.7.8. Spectrophotometry[8]

Spectrophotometric measurements were carried out using a Perkin Elmer UV/VIS Spectrometer Lambda Bio 10 on solutions at 61.5% by weight prepared with purified water which were filtered through a sinter of porosity 4. The absorbance value was taken for a wave length of 420 nm and a length of cell of 1 cm.

9.7.9. Rate of dissolution

The rate of dissolution of the granules was determined by measuring the conductivity of the solutions. The different products were sieved and powders with a particle size of between 420 and 710 μm were retained. For each experiment, the product (50 g) was dissolved in water (100 g) and the mixture was stirred with a mixer at a speed of 1300 RPM. The conductivity of the solution was measured with a Mullard conductivity cell and recorded using a Squirrel data logger. The electrical circuit used is shown in Figure 9.2. It is composed of a power supply, a resistance of 560 KΩ fitted in series with the variable resistance (solution of sugar). The variation of conductivity was taken at the variable resistance.

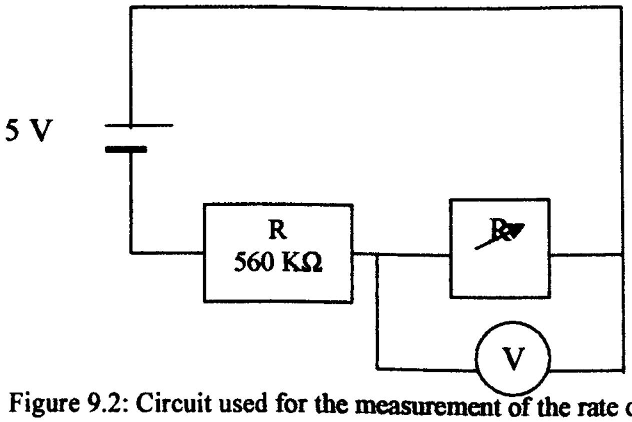

Figure 9.2: Circuit used for the measurement of the rate of dissolution

9.8. Testing of co-crystalline materials in chocolate

9.8.1. Recipes

9.8.1.1. First experiments

Step	Ingredient	% by weight	% of fat	% of free fat	Weight (Kg)
Mixer formulation	Sugar	52.95	0.00	0.00	3.177
	Cocoa butter	18.46	18.46	18.46	1.108
	FCMP	10.59	2.75	0.55	0.635
	SMP	5.29	0.00	0.00	0.318
	Cocoa liquor	12.71	6.99	6.99	0.762
	Total	100.00	28.20	26.00	6.000
Conche formulation	Refined mass	94.43	26.63	24.55	5.670
	Cocoa butter	5.05	5.05	5.05	0.303
	Vanillin	0.02	0.00	0.00	0.001
	Lecithin	0.50	0.50	0.50	0.030
	PGPR	0.00	0.00	0.00	0.000
	Total	100	32.18	30.10	6.000

FCMP: Full Cream Milk Powder
SMP: Skimmed Milk Powder
PGPR: Polyglycerol Polyricinoleate (E 476)

Table 9.2: Milk chocolate recipe for the first batches

Four different batches of chocolate were prepared using the recipe shown in Table 9.2, the "sugar" component being any of the following:

- A co-crystalline material containing 10% of glucose which showed a single peak on the DSC scan with a moisture content of 1.5% (Method 9.3.2.1.)
- A dry blend of sucrose-anhydrous glucose (90/10)
- A dry blend of sucrose-glucose monohydrate (90/10)
- Sucrose.

The ingredients used in the mixer formulation were stirred using a Hobart mixer at low speed for 5 min. Each mixture was then passed twice through a 3-roll refiner. The conching was carried out at 60°C and 40 RPM for four hours in a Minilipp conche (Lipp, Mischtechnik, Mannheim, Germany). About 1/3 of the cocoa butter was added at the beginning of the conching with the rest of the ingredients. For the formulation containing glucose monohydrate, conching was undertaken at 40°C to avoid the release of the water from the glucose.

9.8.1.2. Second experiments

A batch of chocolate was prepared with the same co-crystalline material as previously used (Section 9.8.1.1) but this time the powder was dried to achieve a moisture content of 0.8%. The chocolate was prepared with the following recipe (Table 9.3).

Step	Ingredient	% by weight	% of fat	% of free fat	Weight (Kg)
Mixer formulation	Sugar	52.95	0.00	0.00	3.177
	Cocoa butter	18.46	18.46	18.46	1.108
	FCMP	10.59	2.75	0.55	0.635
	SMP	5.29	0.00	0.00	0.318
	Cocoa liquor	12.71	6.99	6.99	0.762
	Total	100.00	28.20	26.00	6.000
Conche formulation	Refined mass	93.13	26.63	24.24	5.710
	Cocoa butter	6.28	6.29	6.29	0.385
	Vanillin	0.010	0.00	0.00	0.001
	Lecithin	0.49	0.49	0.49	0.030
	PGPR	0.08	0.08	0.08	0.005
	Total	100.00	33.49	31.10	6.131

Table 9.3: Milk chocolate recipe for co-crystalline material at 0.8% moisture

9.8.2. Fat migration experiments

Two batches of Gianduja were prepared with the following recipe (Table 9.4). The sugars used were co-crystalline a glucose-sucrose mixture containing 10% of glucose (Method 9.3.2.1) and pure sucrose respectively. First the sugar, cocoa liquor and the roasted hazelnuts were mixed in a small Stephan mixer (Stephan Söhne Gmbh, Hameln, Germany) at speed 2 for 2 min. The premix was then passed twice through a 3-roll refiner. A first passage was carried out to achieve a particle size of about 100 μm; the second passage was to achieve a particle size of about 20 μm. The mass was stored in a sealed plastic bag at 20°C overnight. It was then conched for 4 hours in a Minilipp conche (Lipp, Mischtechnik, Mannheim, Germany) at 60°C and 55 RPM. The cocoa butter was added after 15 min of conching, the lecithin after 2.5 h and finally the hazelnut oil after 2.75 h. The batches were stored at 45°C overnight.

Ingredient	% by weight	% fat	Processed premix (g)	Final product (g)
Sugar	44.00	0.00	2774	–
Roasted hazelnuts	22.00	13.42	1387	–
Cocoa liquor	16.00	8.64	1009	–
Hazelnut oil	12.00	12.00	–	720
Cocoa butter	6.00	6.00	–	360
Premix	–	–	5170	4920
Total	100.00	40.06	–	6000

Table 9.4: Gianduja recipe for fat migration experiments

A dark tempered chocolate (12 g) was placed in a Petri dish of 5 cm diameter, at the bottom to form a flat layer. The dishes were shaken to remove any air bubble. Once the chocolate was cooled and solidified, a layer of Gianduja (12 g) at 30°C made with sucrose and the co-crystalline material respectively, was placed at the top. The samples were placed in the refrigerator for 1 h and then stored at 23°C and 50% relative humidity.

9.8.3. Viscosity analysis

The viscosity of the different chocolate batches were determined on samples taken at the end of the conching, using a Haake Visco Tester VT550 while increasing shear rates from 2 to 50 sec^{-1} in 3 min and then decreasing shear rates from 50 to 2 sec^{-1} in 3 min. The temperature was maintained at 40°C. Data from both ascending and descending ramps were used in calculation of the Casson parameters with a Haake Rheowin Pro software.

9.8.4. Particle size distribution

Particle size distributions of chocolate mixes were obtained using a Mastersizer from Malvern Instruments. Size distributions were determined as a measure of the relative volume of particles in 45 size bands. The D(V, 0.9) (i.e. the 90th percentile) was taken to characterise the chocolate batches. The chocolate was dispersed in oil until an obscuration of 0.20 was obtained. Ultrasonic dispersion was applied for 2 min to assure that the particles were independently dispersed.

9.8.5. HPLC analysis of the triglycerides

The chocolate samples for fat migration were prepared as follows. The dark chocolate layer was separated from the layer of Gianduja. Chocolate (0.4 g) and hexane (2 mL) were placed in glass tubes. The mixture was vortexed for 2 min with a Gallenkamp Spin-mix and then centrifuged for 3 min at 300 RPM using a Heraeus Labofuge 200. The upper hexane layer (0.1 mL) was placed in a vial and acetonitrile (0.6 mL) and chloroform (0.3 mL) were added. For the standard, 2 drops of cocoa butter in hexane (2 mL) were vortexed and centrifuged. The hexane phase (0.1 mL) was added to chloroform (0.3 mL) and acetonitrile (0.6 mL) in a vial. The triglycerides were separated using a Hewlett Packard pump series 1100. The column used was a 50 cm reverse phase C18 Lichrospher 100-5RP-18EC. The column was at room temperature. The triglycerides were detected with a PL-EMD 950 Evaporative mass detector at 65°C using nitrogen at a pressure of 2 bars. Each time, 5 µL of product were injected. The mobile phase was acetonitrile-chloroform (3:2) at a flow rate of 1 ml/min. The runtime for each experiment was 50 min.

9.9. Testing of co-crystalline materials in tabletting

9.9.1. Particle size analysis

The particle size distribution of the different powders used for tabletting was carried out by sieving using 125, 420 and 710 µm mesh sieves.

9.9.2. Effect of the moisture content

Four different powders were used:

- A co-crystalline material containing 10% of glucose (Method 9.3.2.1)
- A dry blend sucrose-anhydrous glucose (90/10)
- A co-crystalline material containing 90% of glucose (Method 9.3.2.3)
- A dry blend sucrose-anhydrous glucose (10/90).

In each case, the materials were ground using a small Stephan mixer (Stephan Söhne Gmbh, Hameln, Germany) for 1 min at high speed. The co-crystalline materials were further dried for either 1 or 2 h to give products with different moisture contents. These were determined by Karl Fischer Analysis (Method 9.8.5). Magnesium stearate (1% by weight) was added to the four powders before the pressing. The samples were pressed using a Manesty press with 4 sets of dies and punches in place. The machine was set to a pressure of about 6 tonnes. The samples were stored at room temperature in sealed polyethylene bags. The mean crushing strength, weight, thickness and diameter of the tablets were measured using an Erweka Hardness tester on 10 compacts.

9.9.3. Fading of flavour experiments

Five different powders were tested for their capacity to retain flavour:

- A co-crystalline material containing 10% of glucose (Method 9.3.2.1.)
- A co-crystalline material containing 90% of glucose (Method 9.3.2.3.)
- A co-crystalline material containing 10% of glucose and 1% of magnesium stearate that was incorporated during the co-crystallisation process (Method 9.3.2.2.)
- Candy-pac® (a commercial co-crystalline material from Domino Speciality Ingredients)
- Unflavoured Polo granules from production.

The composition of the Polo granules used was 1% of stearic acid, 1% of starch, glucose syrup, icing sugar.

Magnesium stearate (1% weight) was added to samples that did not contain any flowing agent. Mint oil (0.23% by weight) was added to all the samples. The powder and the oil were mixed in a Copley AR401 universal drive unit for two minutes at 428 RPM and then pressed. The compacts obtained were spread on a tray and stored at room temperature at the open air.

In order to determine the amount of flavour retained, compacts were ground using a mortar and a pestle. The resulting powder (2 g) was placed in a vial. The flavours contained in the samples were extracted by Solid Phase Micro Extraction using a SPME Combi-Pal. The incubation time and the temperature were 36 min and 37°C respectively. The agitation speed was 250 RPM. The different flavouring compounds were analysed by Gas Chromatography using an Agilent 6890 Series GC system. The runtime was of 45 min using a 30 m dbwax column. The flavouring components were detected using an

Agilent Mass Selective Detector 5973. Six compacts were taken each time to prepare four vials. Each sample was thus analysed four times.

9.10. References

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Appendix 1: DSC traces of co-crystalline products containing a majority of glucose

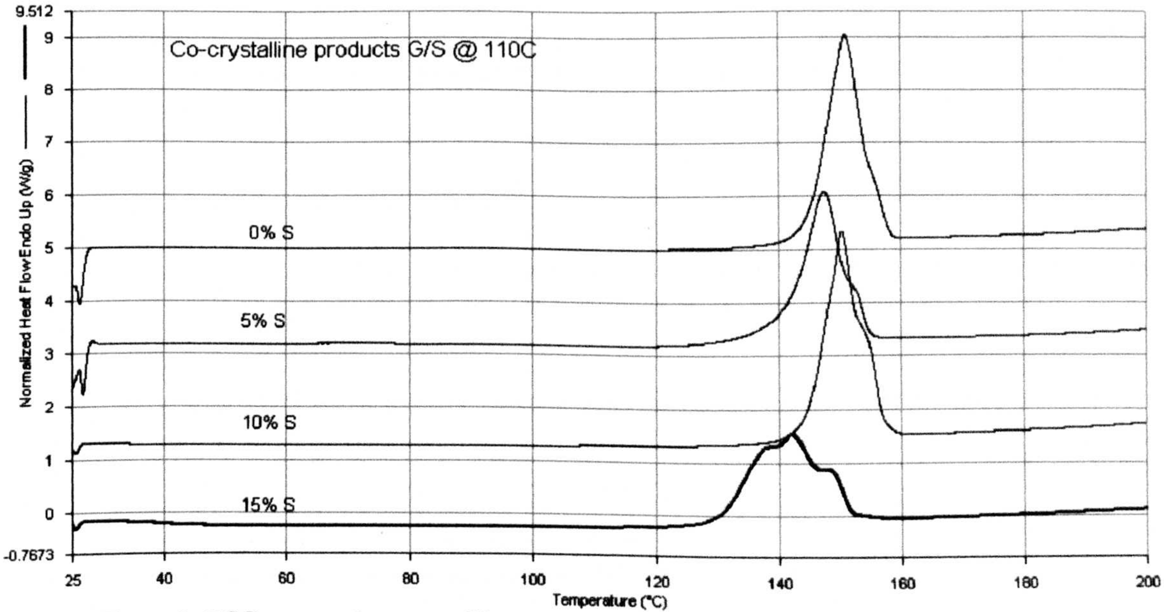


Figure 1: DSC traces of co-crystalline sucrose-glucose products re-crystallised at 110°C

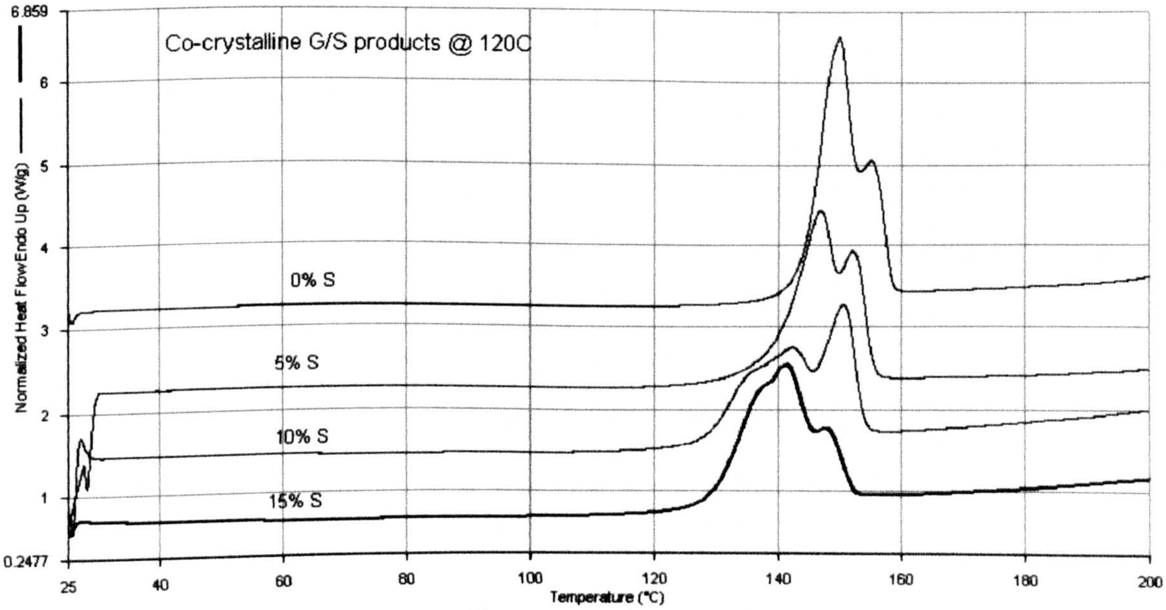


Figure 2: DSC traces of co-crystalline sucrose-glucose products re-crystallised at 120°C

Appendix 1 (continued)

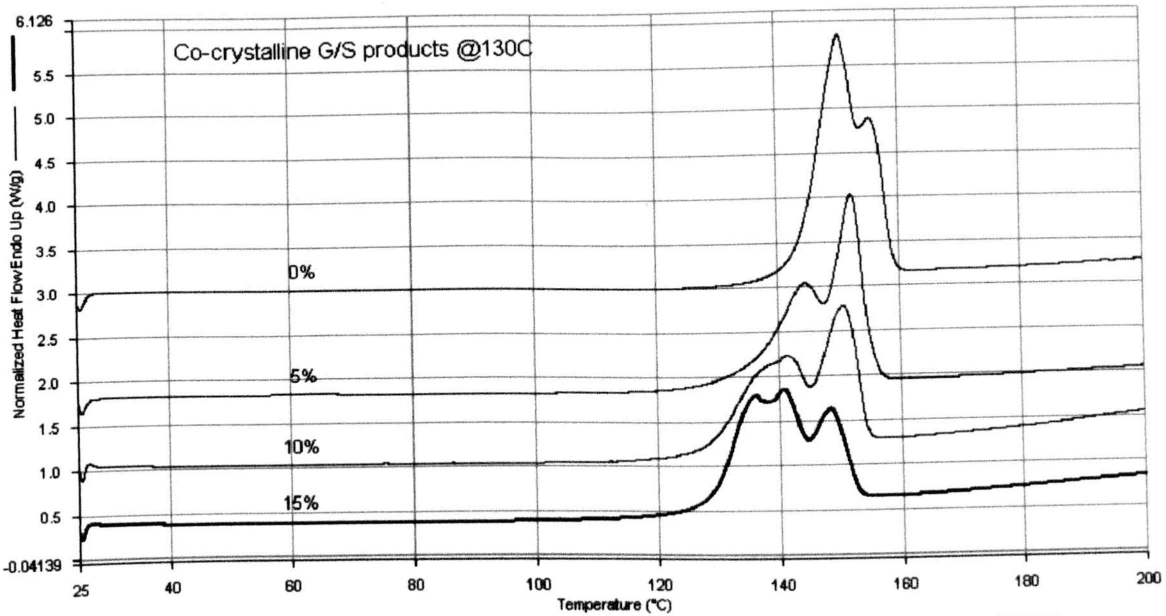


Figure 3: DSC traces of co-crystalline sucrose-glucose products re-crystallised at 130°C

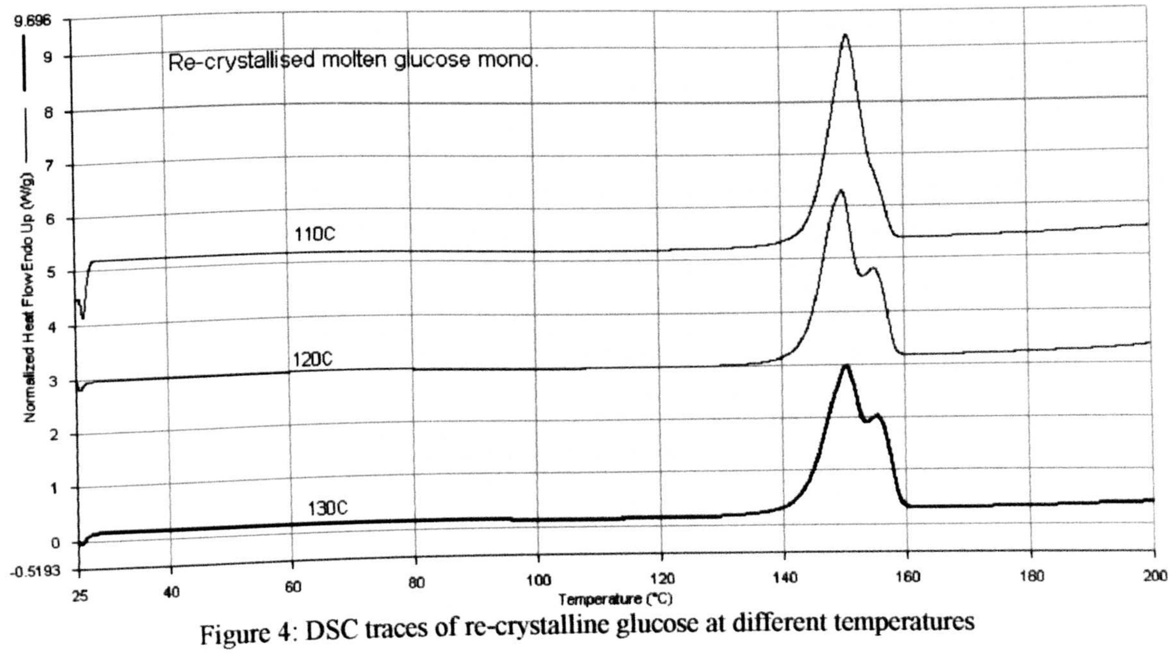


Figure 4: DSC traces of re-crystalline glucose at different temperatures

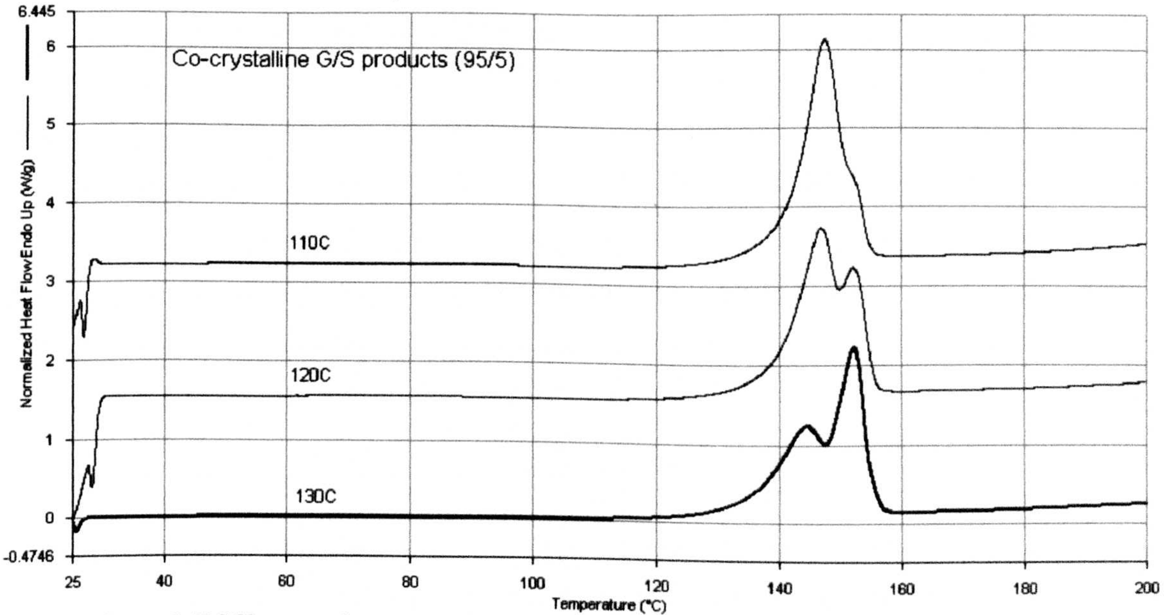


Figure 5: DSC traces of co-crystalline sucrose-glucose products containing 5% of sucrose

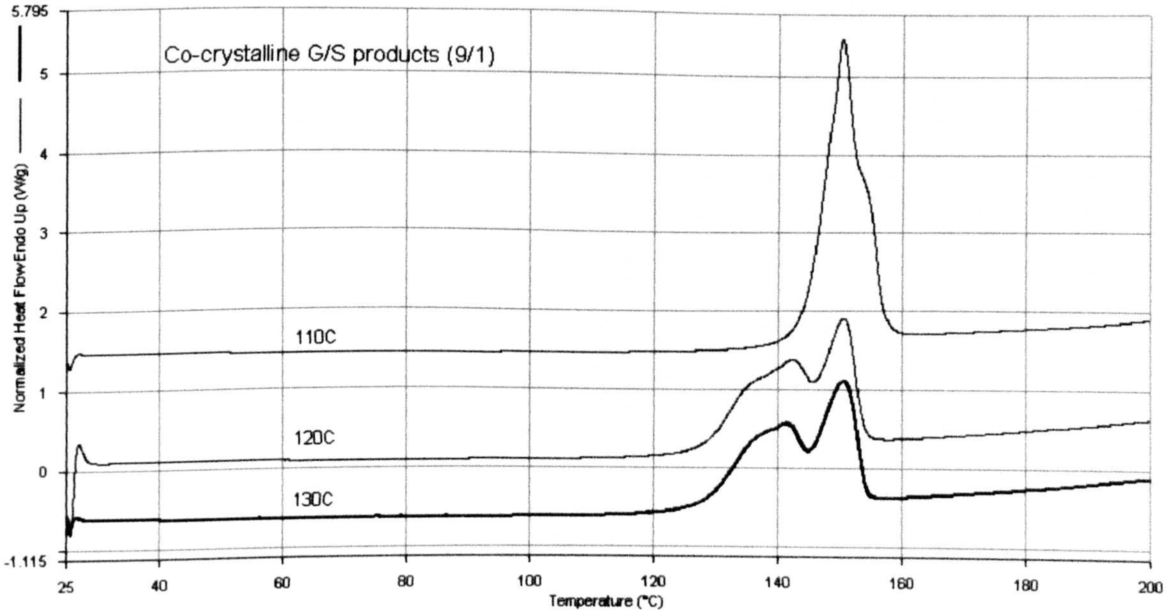


Figure 6: DSC traces of co-crystalline sucrose-glucose products containing 10% of sucrose

Appendix 1 (continued)

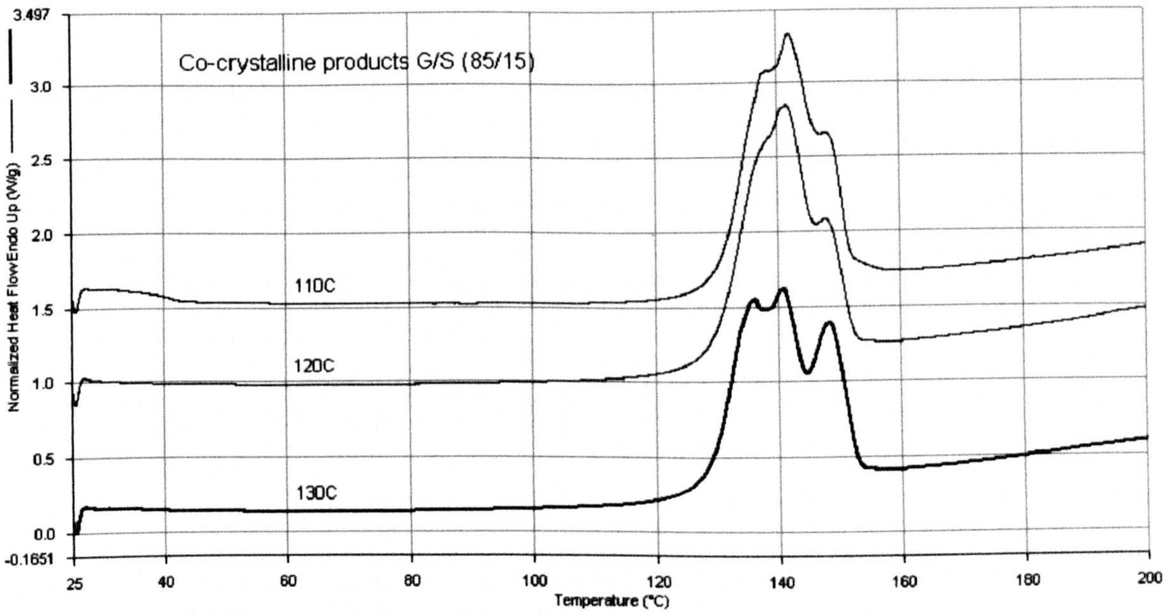
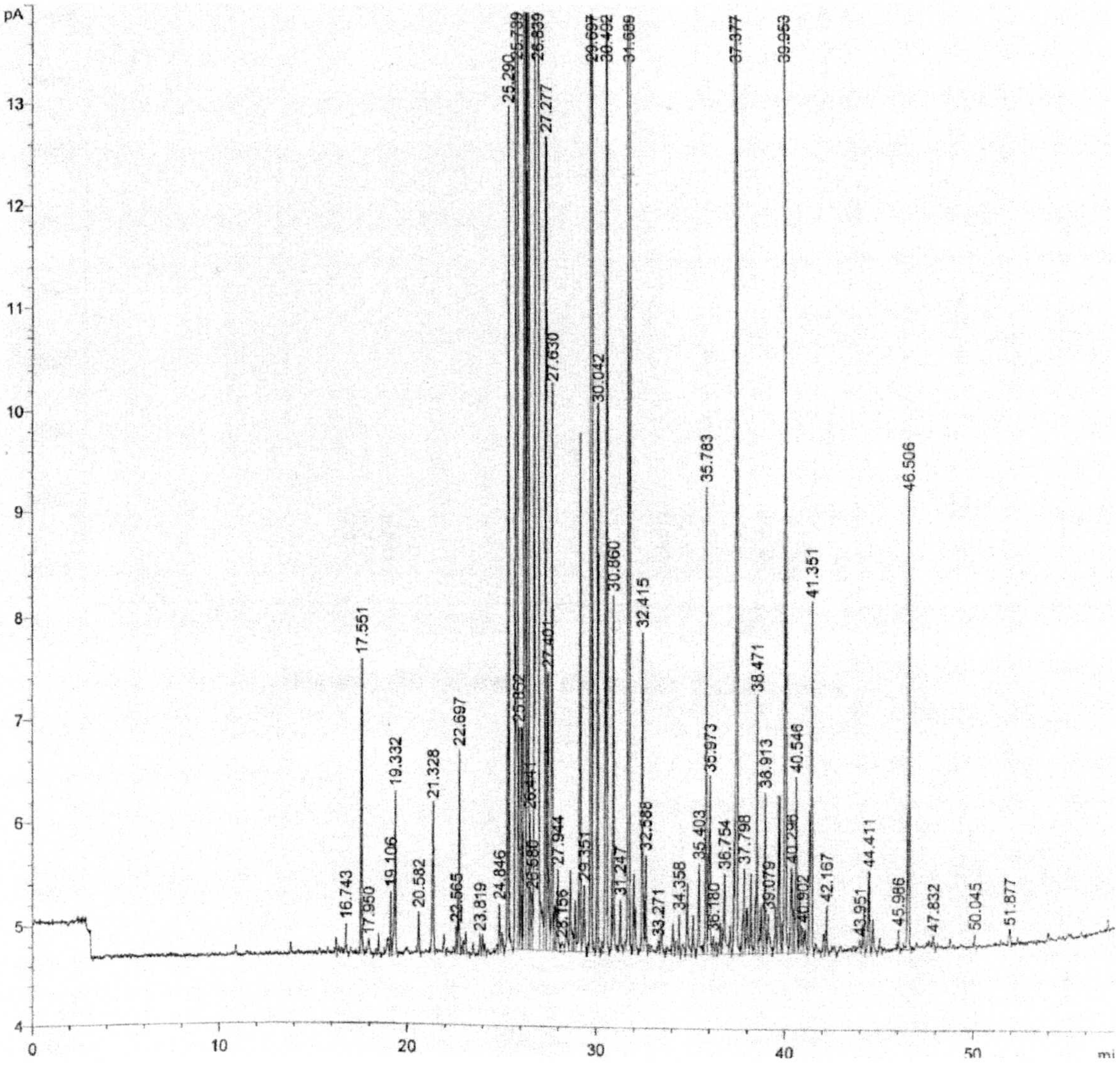


Figure 7: DSC traces of co-crystalline sucrose-glucose products containing 15% of sucrose

Appendix 2: Gas Chromatography trace of mint oil



Appendix 3: HPLC traces of the triglycerides contained in the dark chocolate and the Gianduja

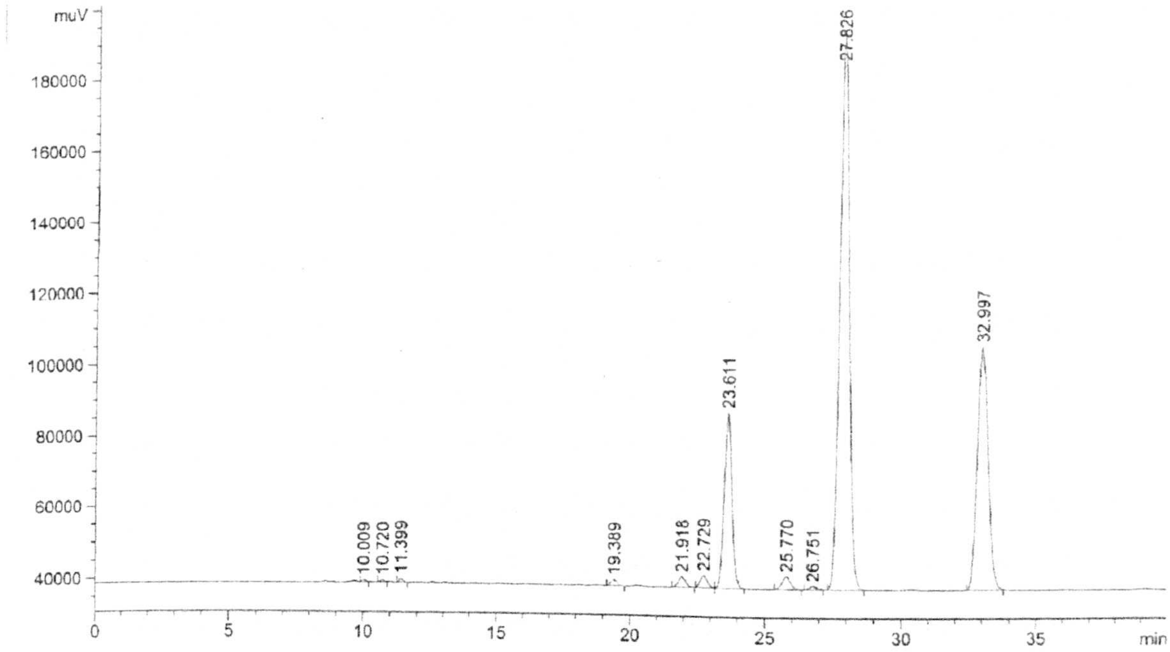


Figure 1: HPLC trace of the starting dark chocolate

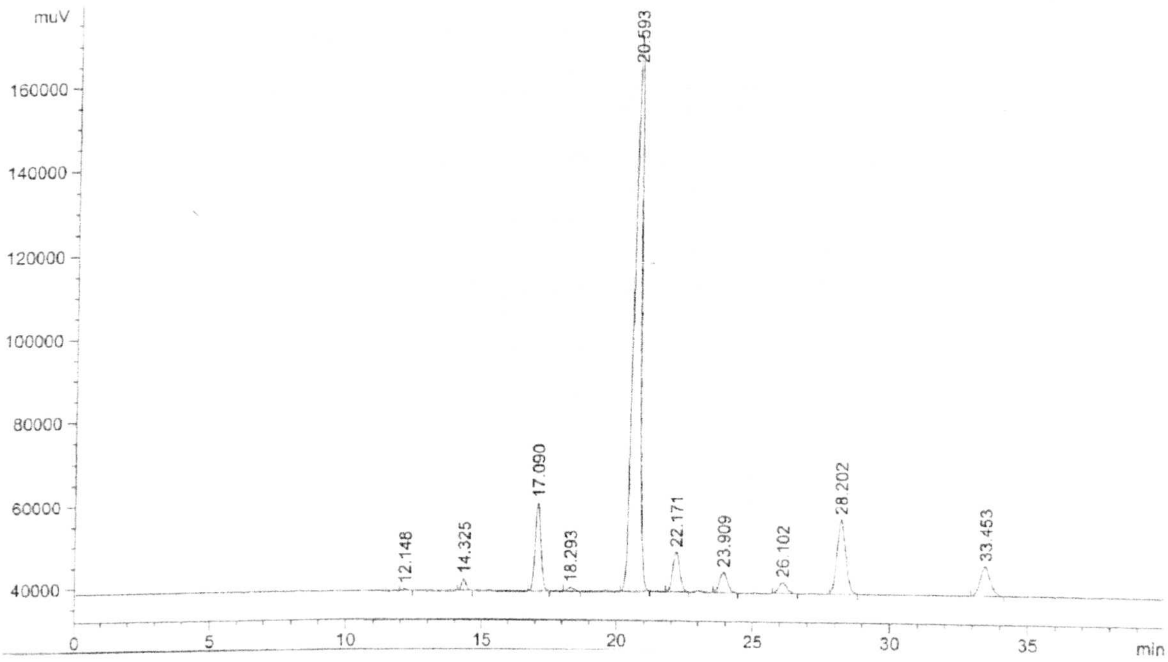


Figure 2: HPLC trace of the starting Gianduja

Appendix 3 (continued)

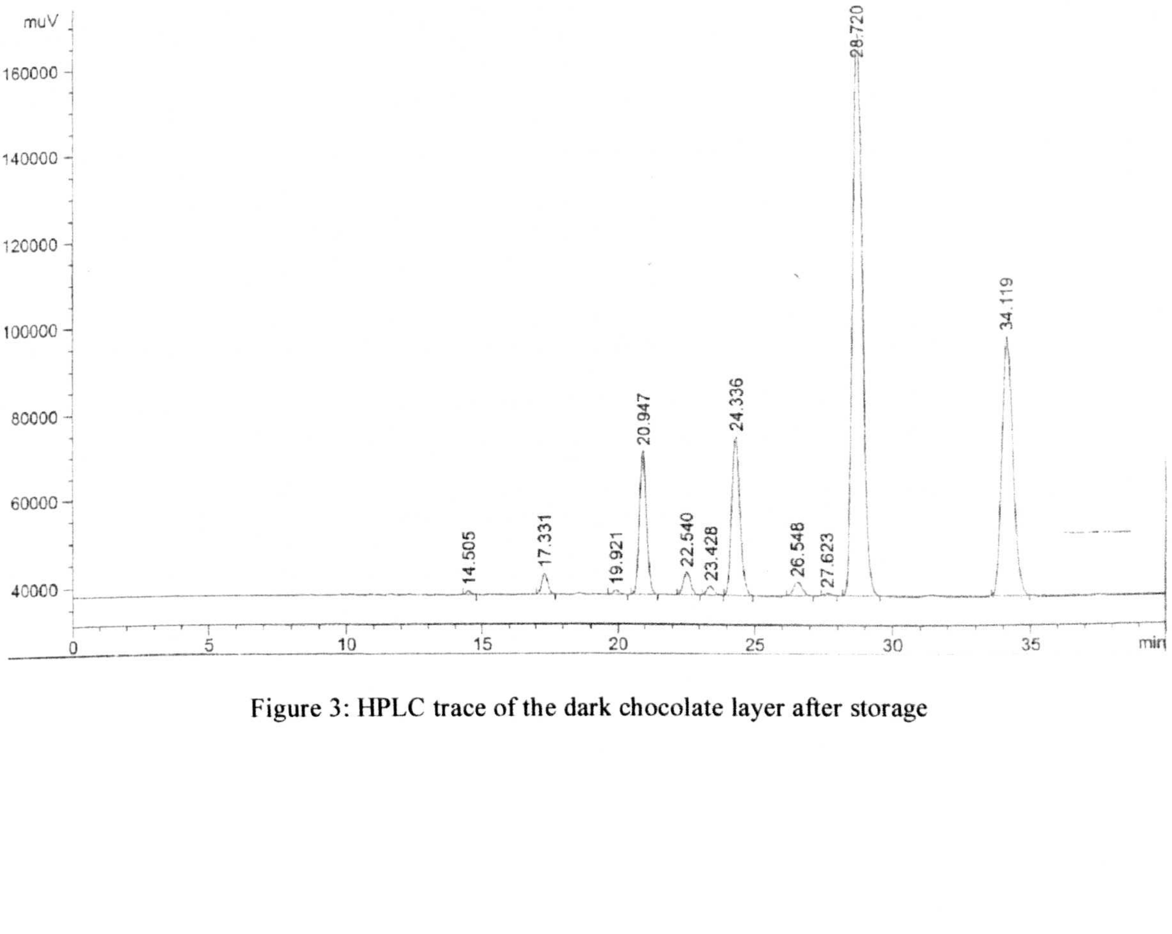


Figure 3: HPLC trace of the dark chocolate layer after storage