The Conditioning of Confectionery Products

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Abstract

The objective of this project was to investigate the conditioning stage of the manufacture of confectionery, using both wine gums and sports mix as model systems.

During conditioning the finished confectionery are left to stand for a period of between 12 and 72 hours before reaching a suitable state to be packed. The conditions are ambient and so the actual temperature and relative humidity vary significantly with both daily and seasonal changes. The three primary aims of conditioning are to reduce stickiness which causes packing problems, allow the samples to strengthen so that they can resist mechanical handling without deformation, and to prevent the sweating of the confectionery after packing. Although conditioning appears to reduce these problems, it does not eliminate them completely and this is felt to be as a result of the variable conditions under which conditioning occurs. For example stickiness is a particular problem during the summer months. At the moment the physical processes which occur during conditioning are not understood and so the conditions cannot be optimised.

Therefore the fundamental aim of the project was to investigate what is happening in this period with the final target of either removing the conditioning stage or reducing it. In order to achieve this, each of the three problems were to be considered separately and the reasons why conditioning currently solves them investigated. Once the physical changes which are occurring had been understood it may have been possible to develop alternative methods of producing conditioned wine gums which are quicker and more cost effective than actually conditioning.

However, due to time restrictions, only the initial stages of this project were completed. Characterisation of four week old sports mixture was undertaken,

using texture analysis, light microscopy and DSC. The collection of this data could be used to ensure that any changes to the process do not result in a change to the product. The changes in texture, stickiness and mass of products were monitored as they conditioned in varying temperature and relative humidity environments. This began to quantify the changes which occur during conditioning. The results appear useful but the trials would need to be repeated to ensure reproducibility, and the range of temperature and relative humidity conditions being tested would need to be extended. The diffusion coefficient was calculated using DVS which would enable some basic modelling of moisture movement within sweets to be undertaken. Phase diagrams were also produced at varying sugar levels. The thesis concludes with a further work section which considers areas of research which could follow on from the results.

Acknowledgments

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Contents

Chapter 1

Introduction

Cadbury manufactures a variety of fruity, chewy confectionery products using starch moulding techniques. Two specific examples which are considered in this thesis are wine gums and sports mixture. Part of the manufacturing process involves leaving the confectionery in storage for between 12 and 72 hours to enable them to reach a state in which they can be packed; this process is called conditioning. This thesis attempted to investigate the physiochemical changes which occur during conditioning in order to understand and then optimise it.

The primary ingredients for these types of sweets are starch and gelatine; hydrocolloids which are miscible at high temperatures but which phase separate and form gels upon cooling. The properties of these components, both individually and when mixed, significantly contribute to the structure and functionality of the confectionery product. Therefore, understanding these polymers, and in particular the phase diagram which describes how the biopolymers phase separate when mixed, is vital in any investigation into confectionery.

Water is also a main ingredient and its distribution is likely to play a key role in all stages of manufacturing, but particularly in conditioning. Therefore

determining a value for the diffusion coefficient is necessary to allow modelling of moisture movement to be carried out.

The processing which these ingredients are subjected to prior to conditioning, particularly stoving, will have a major impact on the state of the product at the start of conditioning and so needs to be thoroughly researched. Understanding the atmospheric conditions, and the variations in these conditions, which are currently used to condition wine gums and sports mix is also a vital starting point in understanding the changes which occur in confectionery during this period.

Fully characterising a conditioned wine gum is necessary to ensure that any modifications which are made to the processing conditions are not noticed by consumers. This can be done in terms of microstructure, texture and moisture content, amongst other things.

Therefore, the literature relating to biopolymers is discussed, as is previous internal and external work relating to the manufacturing process. Some discussion of possible reasons for conditioning is presented on the basis of this literature. The experimental section of the report is then split into two main areas: characterising conditioned confectionery, and monitoring the changes which occur during conditioning. Finally, potential follow up work to the thesis is discussed.

Chapter 2

Processing Information

Starch moulded confectionery has been manufactured for the last 100 years and over this time the process has remained relatively unchanged. Both wine gums and sports mixture are produced at the Sheffield site using a batch processing technique. The manufacturing process is not a quick one, with the transition from raw ingredients to packaged products taking several days to complete.

Originally it was decided that wine gums should be studied as the model system because they are the highest volume unit produced by Cadbury and hence of the most interest to the company. However, during the project the decision was made to change to sports mixture. This was because wine gums have maize starch as one of their primary ingredients and this requires high temperatures and pressures to gelatinise. The pilot plant cooker which is needed to achieve these conditions is difficult to operate by one person and so wine gums are generally made by teams of people. Therefore a product which was easier to make needed to be chosen. Sports mixture is a similar type of product but this is made from potato starch which can be cooked at lower temperatures and so does not require a pressurised cooker. This can even be made in test tubes

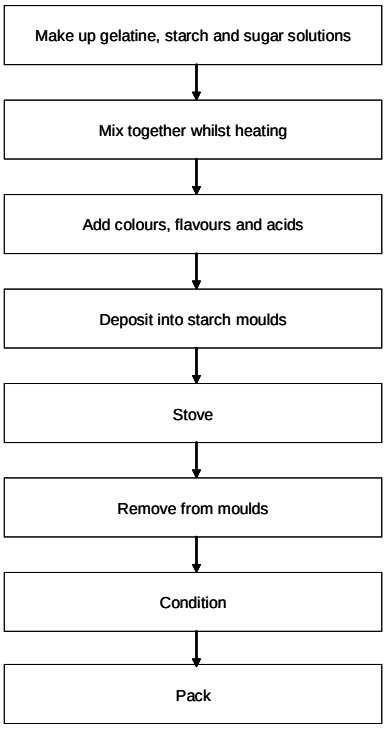

Figure 2.1: Simplified flow chart describing the manufacturing process for starch moulded confectionery

in the lab so was a much more sensible choice. However, a lot of the results in this thesis relate to wine gums rather than sports mixture so many experiments would need to be repeated with sports mixture if the results were to be used for further work.

The manufacturing process for starch moulded confectionery, such as wine gums and sports mixture, is summarised in Figure 2.1 on page 7. Conditions are not stated for confidentiality reasons.

Chapter 3

Literature Review

3.1 Hydrocolloids in Food

3.1.1 Starch

3.1.1.1 Structure

Starch can be obtained from a wide range of botanical sources, including maize, potato and wheat, with the exact properties varying from type to type. The two main constituents of starch are amylose and amylopectin which are both polysaccharide polymers which have glucose units as their monomers. However, their structures are quite different. Amylose consists of linear chains of glucose, each bound by an α 1-4 glycosidic bond. The chain has a small amount of branching, connecting the linear chains by α 1-6 linkages, though these branches only occur every several thousand molecules. Conversely, amylopectin is highly branched. It contains 4-5% of branch points (again α 1-6 bonds), with linear chains only reaching 25-30 glucose units. Its structure makes it a very large

molecule in comparison to amylose. The relative quantities of these two components has a big impact on the properties of the starch, and this is determined by the starch type. Starch can also contain intermediate material such as lipids, proteins and inorganic matter. On average this can make up 5-10% but this value varies depending on the botanical source. (Greenwood & Munro, 1979)

The starch molecules are arranged in granules around a central nucleus (generally just one nucleus, although compound granules do exist which contain several nuclei). The granules can be round, oval or irregularly shaped and range in size from 2µm up to 100µm. Polarised light reveals birefringence (a 'Maltese cross' pattern), implying molecular orientation within the granules, and X-ray diffraction patterns show that they are crystalline. (Blanshard & Mitchell, 1979) Untreated starch will not dissolve in cold water, but in the presence of heat the water is able to penetrate into the granules, causing them to swell and increasing the viscosity of the solution. Upon removal of the heat this swelling is reversible but only until so much water has entered that the granule structure is compromised, allowing the contents to leach out. This is known as gelatinisation, and is irreversible. (Blanshard & Mitchell, 1979) Gelatinisation of a particular granule occurs over just 1-2°C, but each granule is unique and hence full gelatinisation of a whole sample takes 4-10°C. The temperature at the mid point of this range is the gelatinisation temperature, T_g. This normally occurs at around 63-72°C for maize starch, although the presence of sugar and a lower moisture content promotes this temperature. (Greenwood & Munro, 1979)

3.1.1.2 Retrogradation

During gelatinisation, amylose leaches out of the starch granules. Upon cooling, if present in a sufficiently high concentration, this amylose begins to build up

a 3 dimensional skeletal network held together by hydrogen bonds, forming a physical gel. Trapped within the network are amylopectin and any remaining amylose, both dissolved in compartmentalised water, together with the ruptured starch granules. This is the freshly formed gel. However, after gelation the system does not remain static. Instead, upon storage at room temperature, the gel structure begins to change in a process known as retrogradation (Blanshard & Mitchell, 1979). Rather than remaining in solution, the dissolved molecules begin to precipitate out. The amylose does this extremely rapidly, whereas the amylopectin does so more gradually, although for both precipitates the gel is considered fully retrograded within approximately 60 hours. The precipitates either migrate towards the existing amylose network, reinforcing it, or if the concentration of starch is particularly high (40% or more) then the molecules may aggregate with others close by within the compartment to form new layers. (Ohtsuka, et al., 1994) During this process, because the amount of solutes dissolved in the water reduces, the bulk water becomes more mobile (Ohtsuka, et al., 1994) and tends to be expelled from the gel network as it increases in density. This leads to the phenomenon of syneresis, where water is exuded from the gel (Best, 1995). Retrogradation is quickest at around 4°C but it can readily occur up to room temperature. The effect can be reduced by storing at elevated temperatures or by freezing (Kerr, 1950). As retrogradation involves the increase in density of the gel structure it follows that the strength of the gel would be increased. This has been confirmed in various studies (Ohtsuka et al., 1994; Kohyama & Nishinari, 1991).

If wine gums, which leave the stoves at 15°C , are packed immediately following production they are seen to sweat in the bags and are not strong enough to retain their shape during the packing stage. However, if they are stored for 12-72 hours at room temperature the gel strength significantly increases and the

wine gums no longer exude moisture once packaged. Therefore, it was possible that retrogradation and syneresis were occurring during conditioning.

However, upon researching retrogradation in more detail it was discovered that that this phenomenon is inhibited both by the presence of sugar (with fructose more effective than glucose, followed by sucrose) (Kohyama & Nishinari, 1991), low moisture content, and the presence of other gelling agents such as gelatine (Kerr, 1950). The presence of all these factors reduced the likelihood that retrogradation was the problem.

3.1.2 Gelatin

Gelatin[1] is a protein polymer which originates from the skin and bones of animals. It is formed through the denaturation of collagen triple helices to form protein polymers. At a high temperature, in solution, the polymers are arranged in random coils. The polymers interact with themselves via intra molecular bonds, but not each other. When the temperature is lowered the coils form mono helices. If the temperature is lowered further still groups of three of these helices bond together forming triple helices. Physical bonds form between the helices and a three dimensional network which spans the system is formed. Hydrogen bonds have been shown not to play a dominant role in the stabilisation of the triple helix or in stabilising the 3D network; instead Van der Waals forces are thought to be responsible. (Prystupa & Donald, 1996)

The length of time which a gelatin gel has been aged for is a critical factor in determining the strength and so must be specified when defining the gel. The

[1] Eirich (1958) defines *gelatin* to be the family of derived protein and *gelatine* to be the commercially used product which contains 1-3% salts. This terminology has been used in this thesis. Therefore, general theory sections refer to gelatin whereas sections describing trials or experiments refer to gelatine as these were done with the impure commercial product. When referring to literature, the spelling used by the author has been retained.

gel will increase in strength if held at a particular temperature and although the rate at which it hardens decreases with time a constant value has never been observed. However, Ferry (cited in Ward & Courts, 1977) discovered that an approximately constant value could be achieved within a few hours if the gel was pre-cooled and aged at a much lower temperature. The term 'equilibrium gel' was used by Ferry although it does not produce a true equilibrium state since if the gel is heated and re-cooled it would not produce the same state. However, if the gel was cooled and reheated, the same state would be achieved.

The thermal history of a gelatin gel is known to have an effect, not just on the strength of the gel, but also on the formation of the gel network itself. Rapid cooling produces systems devoid of order with weak links formed between entangled polymers as a result of chance interactions. This causes a fine gel network to form. This is completely different from the coarse structure formed during slow cooling made up of regions of ordered, co-operative bonds. Once a stable bond forms, more develop in close proximity whenever thermal motions of chains bring the bonding sites into close enough contact. After the network has spread across the whole system the links are continually strengthened (although as mentioned above this strengthening lessens with age). Most gels tend to have a mixture of both fine and coarse networks since any changes in temperature cause further development of the gel structure (Fonkwe, 2003). For example, if a gel which is matured at high temperatures is cooled, a fine network develops on top of the coarse network, resulting in a gel with a higher strength than one taken directly to the lower temperature since this will just have the fine network. However, on warming the fine network melts first and associated rigidity is lost. Ledward (1966 as cited in Ward & Courts, 1977) showed that there is an optimum pre-maturing temperature of around 25°C.

The rates of cooling have also been seen to have an effect. Lower cooling

rates were found to produce stronger gels that developed during the cooling phase whereas faster cooling did not allow the coil to helix transition to occur until the final temperature was reached (Fonkwe, et al., 2003).

The addition of a small amount of dextran is known to significantly increase the rate of gelation whereas the addition of a co-solute has been seen to increase the gelation temperature from 34°C to 72°C (Fonkwe, et al., 2003). Sugar has also been observed to increase gel strength although the magnitude of this increase depends upon the age and temperature of the gel (Ward & Courts, 1977). Therefore, it is clear that the properties of gelatin gels are significantly affected by the presence of other components and so trying to predict the situation for wine gums based solely in systems of pure gelatin is a difficult task. However, it is likely to give some indication as to the properties seen in a mixed system.

3.1.3 Mixed Biopolymer Systems

3.1.3.1 Phase Separation

Phase separation is the phenomenon that can occur in mixtures of biopolymers, such as starch and gelatine, which are miscible at high temperatures but which become incompatible at lower temperatures. It involves the spontaneous separation of the solution into components, each rich in one biopolymer type, upon cooling of the solution. If sufficient time is allowed so that the system is able to achieve thermal equilibrium, bulk phase separation and creaming will result, so the solution will split into layers with the least dense layer floating on the top.

Whether or not phase separation will occur is dependent upon the relative concentrations of the components. The temperature at which phase separation will occur for a given concentration is illustrated by a phase diagram and

the line which separates the stable one phase system from the region in which phase separation can happen is known as the coexistence or binodal curve, as described by Jones (2002). The temperature corresponding to the maximum in the binodal curve is called the critical temperature. Within the binodal curve there exists another curve, called the spinodal, which defines the region of instability within which phase separation will occur spontaneously (by a mechanism known as spinodal decomposition). The binodal and the spinodal coincide at the critical temperature. The spinodal is determined by the locus of points at which the second derivative of the free energy of the solution with respect to the concentration is zero for varying temperatures. The region between the binodal and spinodal is metastable and hence the solution is not stable but phase separation will not commence via spinodal decomposition. Instead it occurs via a different mechanism called nucleation and growth and occurs either when the system is quenched into the metastable region, or when the quenching through it (by using a concentration away from the critical concentration) occurs at a sufficiently slow rate. It is less common and hence will not be concentrated on. These three regions, the stable, metastable and unstable, together with the curves marking their boundaries, are shown schematically in Figure 3.1 on page 15.

Phase separation occurs within the spinodal as a result of local fluctuations in concentration caused by the random thermal motion of the polymers. In this region a concentration gradient results in the lowering of the free energy of the system so this becomes energetically more favourable. Any small fluctuations, providing they are above a certain wavelength, grow in concentration and in size until bulk phase separation is achieved (Bansil & Carvalho, 1992; Vermeylen, et al., 2006).

Spinodal decomposition occurs in three stages known as the early, interme-

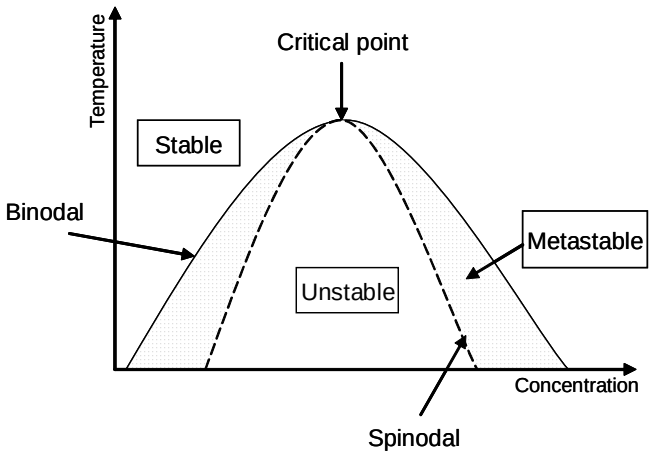

Figure 3.1: Schematic diagram showing the regions of stability for a biopolymer mixture at varying temperature and concentration

diate and late stages. The early stage is described by the Cahn-Hilliard theory (Cahn & Hilliard, 1958). This linear theory predicts that the spatial fluctuations in concentration grow in amplitude at the most energetically favourable wavelength, independently of time. Physically, this corresponds to the concentration increasing exponentially in regions of the size characterised by this wavelength but the size of the region remains constant since the wavelength does not change. This is true only in the early stages of phase separation.

When the peak fluctuations reach the coexisting concentration the wavelength of these fluctuations increases i.e. the domains of high concentration begin to grow in size as well as increasing in concentration in order to minimise the interfacial energy caused by the interfaces. This is the intermediate phase and here the Cahn-Hilliard theory no longer predicts the separation because non-linear terms which were neglected in the theory begin to become important (Vermeylen, et al., 2006).

Finally the late stage can be considered to be the period where the domains continue to grow by self similar growth (Loren, et al, 2001). Self similar growth means that later in time the morphology remains the same but has just increased in size, rather like blowing up part of a photo.

After phase separation by spinodal decomposition is complete, the microstructure continues to coarsen via self similar growth, coalescence, and diffusion (even after gelation). Depending on the concentrations involved the structure of the excluded phase may remain continuous and span the system or it may undergo a percolation to cluster (PTC) transition and convert to droplet morphology. Eventually if the system is left for long enough the system will completely phase separate into two layers and thermal equilibrium will be reached. (Loren, et al, 2001a)

In the case where the system is cooled so that at least one of the components forms a gel, as in the case of confectionery, the phase separation of the system cannot continue until thermodynamic equilibrium is reached. The gelation kinetically traps the system at some non equilibrium stage making the situation far more complex. The final morphology of the system will now depend on the interplay between gelation and phase separation. As a result, thermal history is of vital importance to the microstructure formed.

As well as gelation hindering the process of phase separation, the two processes are also linked by the fact that phase separation can actually promote gelation by locally increasing the concentration of a component to a value at which gelation can occur (Tromp, et al., 1995; Bansil & Carvalho, 1992; Loren, et al., 2001b).

Of particular importance is the relationship between the temperature of phase separation (Tps) and the temperature of gelation (TG). Loren and Hermansson (2000) studied gelatin/ maltodextrin systems which formed a gelatin

continuous phase with maltodextrin inclusions at all the concentrations investigated. They found that by altering the concentrations of the components Tps could be increased, most effectively by increasing the gelatin concentration, although increasing the concentration of the maltodextrin also worked. As a result they were able to study three possibilities: (i) Tps $<$ TG (ii) Tps $\simeq$ TG (iii) Tps $>$ TG, and the effect this had on the final morphology when the system was quenched from 60°C to 10°C.

In the first case the system begins to gel, reducing the mobility of the system and kinetically trapping it before phase separation can completely occur. As a result the maltodextrin inclusions are small, numerous and irregular. When the temperatures are comparable, as in (ii), the phase separation and gelation occur simultaneously, competing with each other. The types of microstructure produced in this case can vary considerably depending on various factors such as cooling rate or residence time at certain temperatures. Lastly, if the phase separation temperature is considerably higher than the gelation temperature then the system will phase separate independently of gelation, exhibiting behaviour similar to non-gelling systems. As a result the inclusions will be large and few and the phase separation clean. Bulk phase separation may be achieved if the residence time above the gelation temperature is great enough.

In the above study all systems were subjected to the same quenching. Clearly, changing the final quench temperature, and how long it is held at this temperature, will also affect the morphology. For example, if the system is similar to case (iii) above but the final temperature to which it is quenched is above the gelation temperature then it is expected that the phase separation should proceed as a normal solution, since the gelation would not have begun. This was clarified by Bansil and Carvalho (1992) on gelatin/ water/ methanol mixtures. They confirmed that the Cahn-Hilliard theory was obeyed at temperatures above gela-

tion, although the peak intensity was found to move to lower wave numbers. This would be consistent with the spinodal decomposition proceeding to the intermediate stage.

Bansil and Carvalho (1992) then found if the temperature was quenched to below TG the gelation resulted in the domain size being pinned at a particular value. This size decreased with increasing quench depth. This concurs with the results of Tromp et al. (1995) on dextran/ gelatin systems; they also found that increasing the quench depth gave rise to smaller inclusions of the discontinuous phase.

Provided that the system is quenched to below the gelation temperature then the relative rates of phase separation and gelation are known to be important to the final morphology. Bansil and Carvalho (1992) showed that if the rate of phase separation is greater than the rate of gelation then the gelation has little effect and the phase separation proceeds independently. For example, this is found to be the case if a gelatin system is quenched to its gelation temperature (around 30°C) simply because gelatin gels extremely slowly at this temperature so phase separation can go to completion before a network can develop (Loren, et al., 2001a). However, if the gelation occurs at a faster rate than phase separation the system will become kinetically trapped away from thermodynamic equilibrium. Again, this result was confirmed by Tromp et al. (1995).

The rate at which the system is cooled also has a major impact and this is particularly relevant to thermal processing. In a series of papers on gelatin/ maltodextrin systems (Loren, et al., 1999; Loren, et al., 2000; Loren, et al., 2001a; Loren et al., 2001b), Loren et al. found that increasing the cooling rate caused a decrease in the final size of the discontinuous phase inclusions. After looking at the effects of cooling rates, different gelatin types, holding times and holding temperatures, Loren et al. discovered that it was the cooling

rate, along with the gelatin type, which had the greatest effect on the final morphology, particularly through the region of 20°C to 30°C where gelation and phase separation were competing. Holding the system above the gelation temperature had the expected effect of allowing the phase separation to progress further unimpeded by the gelation and hence the inclusions were larger and the phase separation cleaner. This effect became more prominent at increased holding times.

The development of the structure in the later stages of spinodal decomposition for a gelling system was studied in detail by Loren et al. in 2001 (2001a). They discovered that quenching at the critical concentration tended to produce a bicontinuous structure even in the later stages of spinodal decomposition. Conversely, those systems which were subjected to the same quenching conditions but at an off-critical concentration could not sustain the continuous structure and underwent a percolation to cluster transition (PTC) resulting in a droplet morphology. This contradicts the result from his 2000 paper (Loren et al., 2000) which stated that the change to droplet morphology was not seen in gelling systems.

The kinetics of phase separation in a gelling system are considerably altered compared to the non-gelling case. For example, hydrodynamic flow is the primary mechanism for causing fast coarsening in the non-gelling case but this is completely suppressed by gelation. Instead, all coarsening occurs solely via the diffusion of individual polymers. This is an important point to note: although gelation kinetically traps the system it does not mean to say it is completely static and so some coarsening can still continue. A major difference is also seen in the length scales of the domains. In the non-gelling systems a narrow range of length scales were seen whereas when gelation occurred the range was far more extensive. As a consequence dynamical scaling, which has been shown to

be useful in the non-gelling case, fails completely (Loren et al., 2000).

Numerous studies have been conducted which prove the importance of the cooling rate on the morphology of systems of this type. Loren et al. (1999) cooled gelatin/maltodextrin systems from 60°C to 10°C at 0.2°C min^{-1}, 1°C min^{-1} and 10°C min^{-1}. As the cooling rate increased the size of the discontinuous inclusions decreased and the interfacial area increased. However, the actual size of the inclusions was also strongly influenced by the type of gelatin used. These results were supported by another paper by Loren et al. in 2000 which looked at the size of the inclusions at varying cooling rates but this time for different concentrations of gelatin and maltodextrin. For the systems studied by Loren et al. in 2000, there was also no percolation to cluster transitions seen in the gelling cases whereas they did occur in the non-gelling systems.

Clearly the development of microstructure in a gelling phase separating system is extremely complex and dependent both on the ingredients, the concentrations and the processing conditions used. This suggests that any variations in either the quantity of ingredients used or in the temperatures and times of processing will have a significant impact on the microstructure of the final product.

3.1.3.2 Phase Separation in Confectionery Products

The microstructure of commercial jelly babies produced by Cadbury in Australia was investigated using light microscopy and transmission electron microscopy by Scuderi (2002). As shown in Figure 3.2 on page 21, they have a continuous starch phase (the lighter phase) with discontinuous gelatine inclusions (darker stain).

Elleman (2006) investigated the microstructure of wine gums as part of a

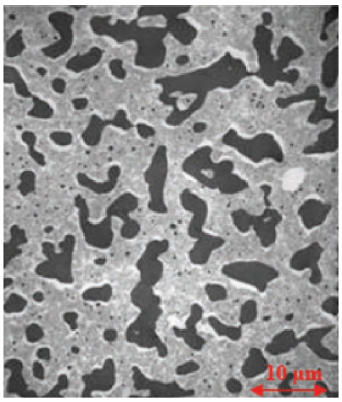

Figure 3.2: Microstructure of a commercial Jelly Bean (Scuderi,2002)

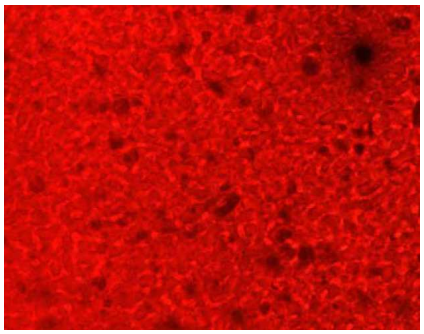

Figure 3.3: Bicontinuous microstructure of a wine gum at a magnification of 410 (Elleman, 2006)

Cadbury internal report and it was discovered that wine gums manufactured in the factory generally display phase separation. The most commonly seen microstructure is a bicontinuous structure where both gelatine and starch span the entire system as shown in Figure 3.3 on page 21. However, this is not always the case.

Discussions with Elleman (private communications, 2007) reveal that phase separation in wine gums is thought to occur above the gelation of starch, which is around 75°C, and above the gelation temperature of gelatine, which is around 30°C. The temperature at which the liquor is deposited is thought to be compa-

rable to the phase separation temperature. Consequently, phase separation will occur predominantly after this as the liquor cools and the free energy reduces, causing demixing. This will continue until the temperature drops to below the starch gelation temperature. This is likely to occur before the trays are put into the stoves at a temperature which is between the gelation temperatures of the starch and gelatine. Although the gelatine will be liquid until after stoving has finished, due to the immobility of the starch phase no more phase separation can occur (other than the coarsening of the structure by diffusion of individual polymers which is an extremely slow process and which will not have a significant impact on the final microstructure).

However, the differences in the observed microstructures may be as a result of phase separation beginning *prior* to depositing, whilst it is still held in the depositing vessel. Elleman (private communications, 2007) suspects that the last two trays in a batch will exhibit the discontinuous phase separation due to the fact that the liquor which enters the depositing vessel first during a cycle will not flow straight through but will coat the inside of the vessel and remain here whilst the remaining liquor passes through (plug flow). This adhered liquor will only deposit once the rest of the batch has been deposited. Therefore it will have been subjected to a significantly longer residence time in the vessel than the rest, providing it with more time to phase separate. In addition, whereas the liquor passing directly through the centre would remain hot, insulated by the surrounding liquor, the liquor next to the wall would be cooling to the temperature at which the jacket is heated, which is below the phase separation threshold. Elleman postulates that this liquor will have a microstructure characteristic of a solution which had longer to phase separate, having progressed from the bicontinuous structure normally seen in wine gums to a droplet morphology, likely to be as a result of a percolation to cluster transformation with

starch as the discontinuous phase.

The importance of obtaining a particular microstructure has not yet been confirmed but based on copious examples from other areas of food processing it seems probable that the microstructure would have an effect. This is currently an area of on-going research and Elleman's initial results suggest that products with a starch discontinuous phase may result in a stickier product and less clean cut face. Reducing stickiness is thought to be one of the main purposes of conditioning so the revelation that it may instead be related to phase separation is particularly relevant to this project. Sticky wine gums lead to production stoppages due to problems with packing so producing a consistent microstructure by more tightly controlling the thermal processing, for example by heating the vessel to a temperature which is above the phase separation temperature, may considerably improve the packing efficiency in the factory.

At the moment there does not seem to be a link between the texture of the wine gums and the microstructure. However, this is difficult to investigate due to the large effect of moisture content on the texture. This tends to be highly variable between batches and so producing wine gums with identical moisture content but different microstructures for comparison is extremely difficult.

3.2 Manufacturing Wine Gums

3.2.1 Stoving

3.2.1.1 Drying

Drying is known to occur in two main stages, the constant drying rate period followed by the falling drying rate period. In the constant drying rate period

any moisture lost from the surface is replaced at the same rate by moisture from the interior. The body therefore dries at a constant rate, limited by the rate at which moisture can evaporate from the surface. This is the same rate that moisture would leave the surface of a body of water. This occurs until the surface becomes dry. At this point the moisture content is at its critical value. This marks the end of the constant rate period. (Van Arsdel, 1963)

As drying progresses, the meniscus of drying gradually moves further into the body. As a result the evaporating water vapour has a longer path to diffuse through before the surface is reached. Therefore, moisture is lost more slowly, and continues to be lost increasingly slowly until drying is complete. This is the falling rate period. During this period, the surface moisture is not being replaced from the interior as quickly as it is being lost. Consequently, it is the rate of internal moisture movement which limits the drying so varying most external factors, such as air movement or the wet bulb temperature will have no effect. Raising the dry bulb temperature is the main option for increasing the drying rate. (Kowalski, 2003)

Internal studies (Brown, 2002) suggest that no constant drying rate period exists for wine gums, instead they enter the falling rate period immediately. As such, factors such as air velocity should not have any effect on the drying rate.

Externally, Ziegler et al. (2003) found using MRI that the moisture loss from a gelatine/starch candy during starch moulding is completely diffusion controlled after the first thirty minutes (a small percentage of the total drying time).

3.2.1.2 Optimisation of stoving cycles

As the necessity for conditioning only arose following a change in stoving procedure, it follows that conditioning and stoving are intrinsically linked. It is therefore necessary to investigate stoving as well as the conditioning part of the manufacturing process of wine gums.

Stoving involves depositing the hot slurry into powdered starch moulds and then immediately transferring these to an oven for a set period of time, followed by cooling. A significant amount of internal work has been done on stoving, successfully reducing the stoving time from the original weekly cycles to less than two days.

The purpose of stoving is to reduce the moisture content of the wine gums from that at which they are deposited, to the final moisture content that is required. Depositing at the higher moisture level gives a sufficiently low viscosity to allow efficient pumping and so that tailing is not generated when the slurry is deposited. The final moisture content has a direct impact on the texture of the final product and an optimal value and an allowable range has been determined.

During stoving the outer layer of the wine gum becomes harder and drier than the interior in a process described as 'case hardening'. This is a topic of considerable dispute in the literature, both internal and external, and a satisfactory conclusion does not seem to have been reached. It may also be a major contributing factor in the need for conditioning. Clearly, as emphasised by Best (1995), the presence of an outer skin has its benefits; it makes the wine gum more robust, allowing it to withstand the physical stresses incurred during packing, and prevents the sweets from sticking together (if this is true it is particularly relevant to the current investigation). The crust is also now a characteristic feature of the wine gum which contributes significantly to the texture, so any change in it (either an increased thickness or hardness of the crust, or its re-

moval) may not be accepted by the consumer. However, the reason it receives so much attention is due to its impact, or perceived impact, on the drying process.

The occurrence of case hardening during stoving was explained by Seagre (1991 as cited in Ziegler et al., 2003) as the result of moisture moving from the surface of the wine gum more quickly than it can be replaced from the interior. It occurs in the initial stages of stoving if the drying rate is too rapid, and is then thought to provide a barrier to further moisture movement from the interior, thus reducing the effectiveness of the stoving process (Ziegler, 2003). A common and seemingly logical answer to this was to try to match the rate of moisture loss from the surface with the rate of moisture migration within the sweet, thereby maintaining the maximal moisture loss throughout stoving. The exterior moisture loss could then be accelerated in the final stages to achieve the necessary crust.

In one of the earliest available internal reports on stoving (Griffin, 1986) it was observed that an increased initial relative humidity (RH) reduced this case hardening and increased the overall drying cycle. Hence it was suggested in this, and numerous later reports, that the optimum stoving cycle should entail a high initial relative humidity which is reduced at the end. However, this was met with some dispute. A later internal report by Bahu (1988) discredited the evidence that the higher humidity reduced case hardening as the RH was not varied independently of temperature. Further to this, the experiments performed in Bahu's report suggested that an increased relative humidity did not affect the drying rate in any way. This is supported by Grover (1947) who also found that for gelatin drying is independent of relative humidity for RH values less than 60%.

Another external source, Cranck (as cited in Van Arsdel, 1963), suggests that the moisture in a body distributes itself in such a way as to maximise the

diffusion of moisture, i.e. the dry crust and moist interior is actually promoting the drying rate by maximising the water potential gradient. It claims that the drying rate is always reduced by a higher humidity. However, this theory is known only to be valid if the surface characteristics of the body do not change over the process of drying, for example it assumes that there is no migration of solutes. Whether this is the case for wine gums is still unclear, though the results from work involving the addition of reducing sugars in wine gums has been explained by assuming that they do redistribute (Eeles, 2005). If this were to be the case then Cranck's argument may not be valid.

Conclusions from internal investigations are somewhat difficult to draw. Most are done on site in working stoves. Many of the conditions are neither monitored nor controlled, for example air velocity. Due to the nature of the equipment, even the factors which are controlled are not kept within strict limits, for example the temperatures in the stoves vary widely depending on the position. Working on site also introduces limitations; frequently experiments could not be performed as required due to stoves being used for other products, or just not functioning due to the break down of machinery.

This issue was studied somewhat more scientifically by Ziegler et al. (2003). They used MRI techniques to follow the moisture profile throughout the drying process, mainly in attempt to compare the drying rate at the candy-starch interface with the candy-air interface. Although previous work had suggested that the air interface was more effective, as Ziegler points out, those tests had only been done in the first four hours of drying and hence could not be considered representative of the whole cycle. Ziegler found a very steep moisture gradient in the first hour at both interfaces, but the rate of moisture loss remained higher throughout the drying at the starch interface. They claim that case hardening was more prominent at the air-candy boundary.

Figure 3.4: Photograph of conditioning area in Sheffield

Another of their articles expands on this, claiming, in line with some of the arguments above, that very dry starch or low RH values provides a larger driving force initially but causes moisture movement to be too rapid and case hardening to occur, therefore causing moisture loss rates towards the end of drying to be less than at higher humidities. They suggest that the moulding starch (as compared with the air on the exposed surface of the wine gums) prevented this initial loss being so high, thereby allowing more moisture to be lost to the starch than to the air over the entire cycle. This suggests that top dressing the trays with starch after depositing could be beneficial to the stoving process.

Other sources attribute the crust more to the incorporation of damp moulding starch into the surface of the wine gum. However, if Ziegler's evidence that the crust is more prominent at the surface exposed to the air, rather than to the starch, can be relied upon, then this seems unlikely.

3.2.2 Conditioning

3.2.2.1 Current Conditions

After the wine gums have been finished they cannot be sent directly to packing, instead they are stacked in trays, as shown in Figure 3.4 on page 28, and stored for anywhere between twelve hours and three days. This is known as 'conditioning'. Not much is known about conditioning. It is rumoured to have been introduced around 12 years ago after a modification to the stoving cycles, possibly following the conversion to a continuous stoving cycle. It is currently thought that one of the main benefits of conditioning is a reduction in sweet stickiness, preventing units from clumping together and then blocking the weighing and packing machines. The possibility that wine gums will sweat in their bags if packed immediately, which would be unpleasant for consumers, has also been suggested as a motivation for conditioning. The most obvious change which occurs during conditioning is the change in texture of the wine gums. They increase in both elasticity and strength and so the explanation that unconditioned wine gums would distort under the pressure of the bags stacked on top of them may contain some truth.

Whatever the original reason may be, the current conditioning regime certainly prevents two out of three of these problems. However, the issue of stickiness remains, particularly in the summer months.

Conditioning is a time consuming operation, and one which requires a substantial amount of space in the factory. A limit to the space available limits the amount of wine gums produced and hence the amount packed and sold. It is also difficult to deal with logistically in the factory and it is common for wine gums to be stored for longer than the recommended conditioning time, frequently resulting in wine gums being over conditioned and then rejected due to a fall in

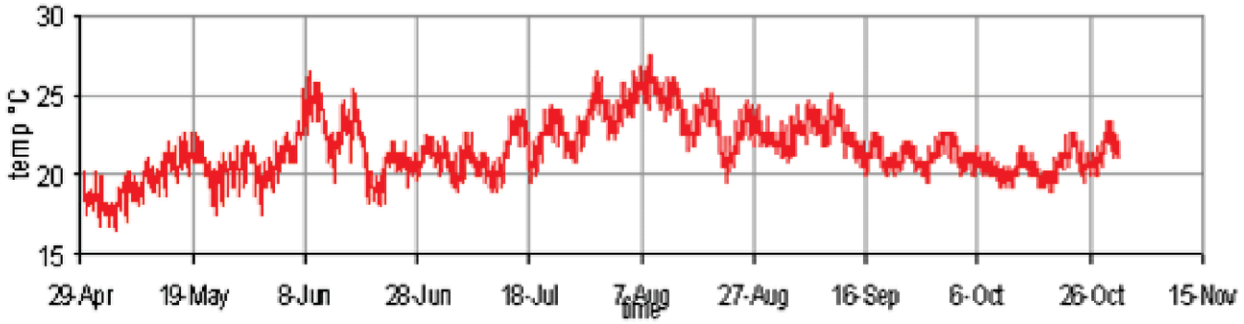

Figure 3.5: Temperature variation over time in conditioning area (Trippass, 2005)

quality. As it is not even consistently preventing stoppages during packing it is clearly an area of processing which requires attention and one which may be creating more problems than it is solving.

The areas where the wine gums are conditioned are left at ambient conditions and so the exact temperature and relative humidity varies both daily and seasonally. The summer is particularly bad in terms of relative humidity variation and this is thought to be increasing the packing problems. The temperature and relative humidity was monitored in 2005 between the months of April and October (Trippass, 2005). Figure 3.5 shows the temperature variation. It can be seen that there is a vast variation, ranging from 16°C to 27°C . Figure 3.6 shows the variation in the relative humidity for the same time period. This also varies significantly, ranging from 32% to 86%.

Until further tests are conducted it will be assumed that conditioning has been introduced to solve the problems of deformation, sweating and stickiness. The main objective of this project is to establish the physiochemical changes which are occurring during conditioning which enables standing in a room at ambient conditions to be relatively effective at solving these problems. Although it is possible there is just one physiochemical change which is occurring which

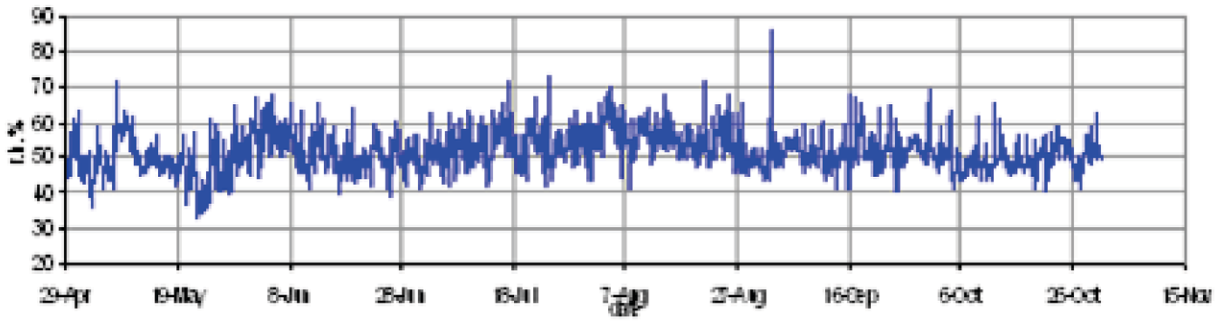

Figure 3.6: Relative humidity variation over time in conditioning area (Trippass, 2005)

solves all of these problems simultaneously, it is also possible that they all have different origins and hence different solutions and that it is a coincidence that conditioning solves them all. Therefore, the three problems will be considered individually.

3.2.2.2 Sweating

It is a well known fact that wine gums are hygroscopic materials and so if they are stored above or below their equilibrium relative humidity (ERH) they will lose or gain moisture respectively. This was demonstrated by Trippass (2005) in a report on conditioning. Trippass then investigated the moisture changes in wine gums during conditioning by choosing a sample of wine gums from the finishing line and then monitoring them as they conditioned over a 4 day period. This was done by weighing them every hour for the first 10 hours and then once a day for the remaining 3 days. It was found that the wine gums gained weight for the first 4 hours, after which their weights remained constant for a few hours. However, the weights then fell again over the next few days, ending up slightly below the starting weights.

Since the conditions were not monitored it is possible that the RH in the conditioning area decreased in the latter days of the experiment and so although the wine gums initially reached equilibrium after 4 hours, they were then forced to re-equilibrate each day as a result of variations in the ambient conditions. However, the fact that wine gums generally become too dry if they are conditioned for more than 3 days suggest this is not the case. A more likely explanation is that the initial moisture uptake is due to the extremely dry crust which is present as a result of stoving. The crust then equilibrates with the atmosphere, preventing any further uptake, after which the wine gum dries. If left exposed to the atmosphere it will reach equilibrium, resulting in an overly dry and hard candy. However, if it is packed, because the system is closed any moisture which leaves the wine gum increases the local RH in the bag so the final equilibrium moisture content of the wine gum is higher than if the wine gum was not packed. The moisture profiles in each case are shown schematically in Figure 3.7 on page 33.

If this is the case, and the wine gums do not completely equilibrate before packing this would be in disagreement with current assumptions about conditioning. For example, Nelson (1995) states that conditioning is required to allow sweets to equilibrate with the packing room RH to prevent sweating in the bags. In Trippass's report, the moisture content after 1 day was slightly higher than the moisture content immediately following stoving, after 2 days it was equal, and after 3 days it was slightly below. Since wine gums can be successfully bagged anytime from 12 to 36 hours without resulting in sweating the small difference in total moisture content obviously does not cause the problem. Further to this, if a wine gum is packed after 2 days, the total moisture content of the system (the bag containing air and the wine gum) would be identical to the system if the wine gum was packed immediately after finishing. Although

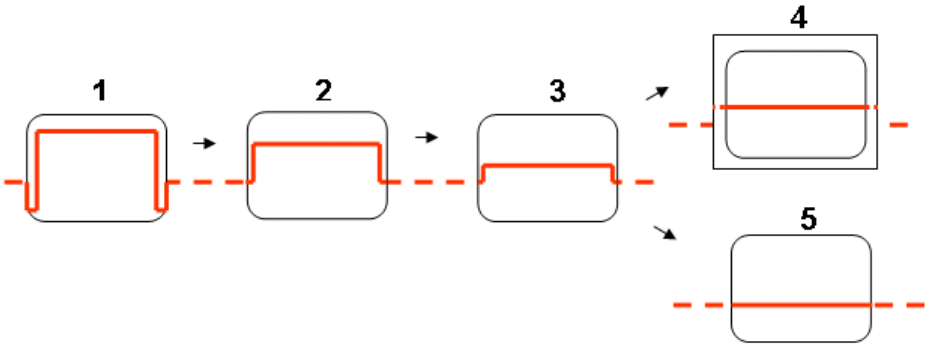

Figure 3.7: Schematic diagram showing the possible changing moisture profile in a conditioning, and then bagged, wine gum. 1) Dry crust, moist interior. 2) Moisture movement into crust from both air and interior until crust equilibrates with ambient RH. 3) Wine gum dries. 4) If sealed in a bag, the ambient RH increases and the wine gum reaches equilibrium at a value where candy is still sufficiently moist. 5) If not bagged, wine gum equilibrates with original RH value producing an overly dry and hard wine gum.

the moisture distribution would initially be different, there seems to be no reason why both systems should not equilibrate to the same state, if given enough time. This suggests that there is another difference between the conditioned and unconditioned wine gum which causes the problem.

One possibility is the temperature of the sweets. Immediately after leaving the stoves they would be at 15°C. If they were packaged in this state they would draw heat from both the bag and the air. If the bag has a low specific heat capacity it may lose the heat rapidly, cool down to below the dew point and cause the moisture in the air to condense onto the inside of the bags. Clearly it would have to be a hot, humid day to result in such a high dew point therefore if this was the reason why sweating occurred it would not have been seen in the winter. Unfortunately, the time of year when conditioning was introduced is not known. This needs to be tested.

3.2.2.3 Deformation

If wine gums are orally tested throughout the conditioning process, it is the textural changes which are the most apparent. Immediately following stoving the wine gums are very soft inside and stick to your teeth during chewing. As conditioning proceeds, the wine gums become firmer and easier to eat. The fact that wine gums will deform during packing if they are not conditioned is thought to be one of the primary reasons for the introduction of conditioning.

However, Trippass did a test of springiness to assess the rate at which wine gums regained their shape after being deformed and found no correlation with conditioning time and found an extremely large variance at all times tested. This was also true for the peak force needed to deform the wine gums. It is therefore possible that deformation would not be a problem even if wine gums were not conditioned. However, a difference in texture is clearly evident from eating them so it may be that the tests performed by Trippass were just not suitable for detecting the changes which occur.

Moisture content and texture are thought to be closely linked with a higher moisture content giving rise to a softer product. This can clearly be seen by the fact that wine gums dry out and become hard after more than 3 days of conditioning. However, this is unlikely to be the only reason for their increase in strength since it is also known that wine gums continue to harden throughout storage after packing, reaching their optimum texture after 4 weeks. Since the wine gums dry out so quickly when being conditioned it is unlikely that it takes 4 weeks for them to equilibrate with the air in the bag. Therefore there must be another mechanism causing the wine gums to change texture during storage. This is thought to be the development of the gelatine gel network.

Although numerous reports have been written on stoving, they all consider the most effective way to heat the wine gums in order to lose the desired amount

of moisture in the quickest time. The cooling cycle at the end, and the profound effect it has on the gelation of gelatine, appears to have received little attention. However, as was described in section 3.1.2., the strength of a gelatine gel is extremely dependent upon its history, both in terms of age and thermal processing so it is likely that any change to the stoving cycle, particularly the cooling part, would significantly alter the wine gum texture even at an identical moisture content. Gelatine sets particularly slowly and it is likely that although the eight hour cooling period may be long enough for the formation of a basic structure, it would not be enough for the network to mature and develop thoroughly. The wine gum would need to be held for a longer period of time before it was strong and elastic enough to withstand mechanical stresses.

This hypothesis is supported by the fact that during final solids depositing trials within Cadbury, the deposited liquor required 12 hours to set and develop the correct gel strength, despite already possessing the correct moisture content. Therefore, it seems likely that the conditioning period is required to allow the development of the gelatine gel network. If this was true then since the structure of gelatine gels is particularly sensitive to processing conditions it may be possible to obtain a similar network just through stoving, without the need for further storage, by manipulating the cooling cycle.

However, if conditioning does harden the wine gums simply due to changes in moisture content, Trippass's gravimetric results show the problem is one of equilibration rather than moisture loss since the fully conditioned wine gums were similar in weight, and therefore total moisture content, to an unconditioned wine gum. Before equilibration the interior of the wine gum would be moist and the crust much drier but after conditioning the moisture is thought to be more uniform. Consequently, the interior would be slightly drier and therefore harder.

The temperature variation in the conditioning area is likely to impact the

texture slightly whichever method is found to be dominant in developing the texture. Firstly, it would obviously affect the temperature of the wine gum and hence the internal diffusion rate so the moisture in a wine gum stored at higher temperatures would equilibrate more quickly and so require less conditioning. Secondly, the formation of the gel structure is temperature dependent so different aging temperatures would lead to the formation of different gel structures and consequently different strengths of gels. However it is likely that 12 hours at any temperature seen in the conditioning area would be sufficient for the formation of a strong enough gel network, or for sufficient moisture equilibration.

3.2.2.4 Stickiness

Clearly, wine gums will be sticky to some extent under any storage conditions since they are largely composed of sucrose and glucose syrup. However, after conditioning this stickiness does not normally pose a problem, for example, throughout the winter months wine gums are packed without problem. It is only sporadically during the summer that the sweets become so sticky that units clump together resulting in blockages in the weighing and packing machines. Because it is known that the RH and temperature are so variable during the summer, a common conclusion which has been reached is that particularly high values of RH lead to wine gums absorbing moisture from the atmosphere making them stickier. This was the basis of the report done by Trippass (2005) on conditioning. She monitored the conditions in the conditioning area (the results were shown in figures 3.5 and 3.6) showing that the RH rose above 70% on at least 5 occasions during the three month period considered, and demonstrated that wine gums lose or gain weight depending on the storage RH, but could not prove the link between absorbing moisture and an increased level of stickiness.

A test of adhesiveness was done on the QTS Texture Analyser, testing the work required to pull the wine gum away from a surface and there was no decrease in the adhesiveness over the course of conditioning. (The adhesiveness values were not compared at different RH values). A very large variance in the measurements was seen at all times.

Another report done on conditioning (Eeles, 2005) assumes that reducing the stickiness of sweets is the sole reason for conditioning and so the authors vary a number of factors in an attempt to reduce this stickiness. A method of quantifying stickiness is developed; two sweets are pressed together and the peak force required to separate them is measured. Experiments were done to consider the effect of invert sugar by examining batches containing 0%, 3% and 6% invert sugar, the effect of top dressing with starch during holding, and lastly the effect of the storage relative humidity.

It was found that gums which had the top surface covered with starch prior to conditioning were less sticky than those which were not. This was in agreement with the fact that the top surface in a normal batch (i.e. top surface not covered with starch) was found to be stickier than the bottom surface.

Surprisingly, it was found that increasing the amount of invert sugar actually reduced the stickiness. The difference was not significant for the 0% and 3% cases but was significant in the 6% case. This was surprising since invert sugar is a humectant and so normally associated with withholding water and so increasing the stickiness.

Increasing the relative humidity at which the gums were stored resulted in a decrease in moisture loss as expected. Less expected was the fact that wine gums stored at RH values as high as 74% lost moisture, despite the fact that this was thought to be above the ERH (63%). The RH did not correlate with stickiness. For example, with the batch containing 3% invert sugar the wine

gums held at 44%RH were the stickiest whereas those held at 25-33%RH and 76%RH were comparable in stickiness.

Higher RH conditions also seemed to produce a smoother surface than lower RH values. This is thought to be as a result of less shrinkage because of the lower loss of moisture. The explanation given for the higher RH values decreasing the stickiness was the fact that a higher RH would be more comparable with the RH in the centre of the wine gum. This would lead to a higher permeability and so would allow more mobility of the sugars within the sweet. It is therefore proposed that the sugars migrate to the centre of the sweet leaving less at the edge and therefore reducing the stickiness.

They concluded that moisture loss at the surface was an important mechanism in reducing stickiness since moisture was lost and stickiness reduced over the conditioning period. They supported this assumption by the increase in stickiness suffered by the top surface compared to the bottom surface. They claimed that since these surfaces were subjected to different drying conditions during the holding stage this supports the theory that different surface moisture contents lead to a different level of stickiness.

Eeles concludes that surface drying causes stickiness to decrease; this would imply that conditioning at Sheffield does not prevent stickiness since Trippass' results suggest that wine gum surfaces gain moisture during conditioning.

It is also worth mentioning that the Eeles' trials were not conducted on sweets which had been stoved, instead they deposited final moisture content sweets in starch preheated to 50°C, cooled them to ambient for 16 hours (the 'holding time') and then conditioned them in a room for ambient temperature for 24 hours, after which the stickiness was seen to plateau. It is likely that the surface of the Sheffield wine gums would be significantly drier than this after being stoved at around 70°C for 20 hours and then cooled for 8 hours.

Therefore, whether conditioning prevents stickiness or not is questionable. The main recommendation from Eeles' report, since it was the most easily implemented, was to top dress with starch during the holding time. As well as increasing surface drying, this would also create a rougher surface and would be expected to lead to a reduction in adhesion. For the Sheffield factory this would mean top dressing during stoving. As it was emphasised by Ziegler (2003) that this may improve drying efficiency, this may prove useful on both counts.

As Eeles considers this to be the most effective way to reduce conditioning it raises the interesting question of why jelly babies require conditioning since they are covered in excess starch as part of the finishing process. Again, this supports the view that the more important role of conditioning is to develop texture.

Overall, the stickiest products were found after storage at around 50-60% RH. By looking at the data obtained from the conditioning area it can be seen that the humidity is most commonly in the range 40-60%. Although packing problems do tend to be more severe during the summer the machines are not constantly blocked and so it is likely that the stickiness found in Eeles' experiments would not be enough to cause these stoppages. Despite the broad correlation of total moisture loss and stickiness over the duration of conditioning, Eeles' results showed no connection when individual cases were considered, as illustrated by the lower stickiness of the batches stored at high RH.

A more important factor relating to stickiness is likely to be moisture on the surface of the candy rather than whether moisture is gained or lost as vapour. When wine gums are stored under high relative humidity although they may absorb the water vapour this does not imply that the water is deposited at the surface. (In fact, in the experiments done by Eeles the wine gums lost moisture during conditioning at all RH values tested, even at 75% RH). Therefore an

alternative explanation of why the variation in RH in the summer leads to excessively sticky sweets may be condensation rather than moisture absorption. When the temperature of a body is at or below the dew point of the air under the current conditions, water will condense from the air onto the surface of that body. The dew point is related to the relative humidity and the temperature of the gas by equation (3.1):

$$T_D = \frac{b\gamma(T, RH)}{a - \gamma(T, RH)} \tag{3.1}$$

where $\gamma = \frac{aT}{b+T} + \ln RH$, a=17.27, b=237.7°C, T is the temperature in degrees Celsius which must be between 0°C and 100°C and RH is relative humidity defined as a fraction rather than a percentage. This predicts the dew point temperature to an accuracy of ±0.4°C.

Wine gums are cooled to a temperature of 15°C after stoving and are then de-starched using ambient air, and are then held at ambient conditions. During the summer when the ambient temperature and relative humidity are particularly high, the dew point can be above 15°C. Therefore, water may condense onto the surface of the wine gum which would dissolve any sucrose and glucose present there, making the surface sticky. This will be considerably stickier than the natural stickiness of a stoved wine gum and hence could be enough to bind wine gums together into clumps causing blockages. This would explain why Eeles did not see an increase in stickiness at high RH. The highest temperature/ RH combination was 20°C /74% RH leading to a dew point of 15.2°C. Although the exact temperature of the wine gums are not specified when they enter the conditioning room he does say that they are cooled to 'ambient'. He later says that the ambient temperature in the texture analysis room was 18/19°C therefore it is reasonable to assume that the wine gums were cooled to a temperature similar to this. Consequently they would be above the dew point temperature so

no condensation of moisture would occur therefore the sweets would not become unreasonably sticky.

As stated in section 3.1.3.2., Elleman (2006) has found that a morphology characterised by a discontinuous starch phase results in stickier sweets. She proposes that this may be due to the fact that the shorter chained sugars tend to dissolve in the continuous gelatine phase and the presence of these near the surface tends to result in a stickier sweet. Normally these sugars are trapped due to the continuous starch phase but as a result of it becoming discontinuous the short chained sugars are more able to migrate to the surface. (It is interesting that both Elleman and Eeles attribute the stickiness problem to a migration of sugars and yet one believes it is the migration to the surface and the other believes it is the migration to the centre. MRI could be used to study the migration of solutes to settle this dispute). As described in section 3.1.3.2., this phase separation is believed to occur in approximately the last two trays of every batch and hence all of these would be stickier than the standard. If this was the sole reason for the packing problems experienced at Sheffield, blockages would occur for some wine gums in every batch, which is not seen to be the case.

It is possible that the actual stoppages occur when both of these situations arise together i.e. when moisture condenses on the surface of discontinuous phase separated products. The discontinuous morphology would allow the sugars to be more mobile and hence more sugar would dissolve in the moisture which has condensed on the surface leading to a higher degree of stickiness. This may explain why not all of the wine gums which are conditioned on a hot and humid day stick together and cause problems.

3.2.3 Pilot Plant Samples

Originally it was anticipated that wine gums could be produced on Bournville's pilot plant as part of the investigation. This would mean samples could be prepared in Bournville as and when necessary, and made under varying conditions rather than being restricted to working at Sheffield and only using the standard factory wine gums. Therefore training on the pilot plant three-in-one cooker was undertaken. However, in order for any results obtained on the pilot plant to be transferable to the commercial situation it must be confirmed that wine gums produced under standard conditions by both of these methods are sufficiently similar.

An internal Cadbury report by Elleman (2006) investigated this, using both light microscopy and transmission electron microscopy to ensure the microstructures of the commercial and pilot plant products were comparable. It was discovered that they were not. Wine gums manufactured in the factory generally display phase separation. The most commonly seen microstructure is a bicontinuous structure where both gelatine and starch span the entire system as shown in Figure 3.3 on page 21.

Conversely, wine gums made on the pilot plant rarely phase separate. Products made on the Bournville jet cooker very occasionally exhibit phase separation and partial phase separation was seen once in wine gums cooked at the highest temperature on the Lille pilot plant cooker. If the origin of these differences can be understood then it is possible that changes to the pilot plant process could be made in order to ensure the factory microstructure is recreated. If this was successful then subject to confirming that pilot plant products are comparable to factory products in other ways, for example moisture content and texture, then the pilot plant samples could reliably be used as part of investigations. However, if the pilot plant conditions cannot be altered then the decision

of whether to use it to create samples has to be based on the sensitivity of the particular experiment, i.e. if the result of the trial is likely to be affected by a difference in microstructure. For example, despite Elleman's discovery that the microstructures were different, the macroscopic properties of the wine gums did not appear significantly different and so the Bournville pilot plant was used in the next project regardless. However, for the trials undertaken in this thesis it was decided to use factory samples only.

It is worth bearing in mind that any wine gums manufactured, whether that is on the pilot plant or in the factory, are subject to quite large variations and that 'ideal' wine gums are impossible to achieve. Even if factory samples are used, they will differ depending on a huge variety of factors, for example their position in the stove, or whether they were part of the first or last tray to be deposited.

Chapter 4

Materials and Methods

4.1 Characterisation of Texture

4.1.1 Texture Analysis

There are a wide variety of texture analysis techniques which can be used but stress relaxation testing was thought to be the most suitable. Stress relaxation is the phenomenon experienced by polymers whereby the force needed to maintain a specific deformation decreases over time. This is as a result of the polymers rearranging to dissipate the energy and reduce the stress. In order to test for this property, the sample is compressed to a given deformation using a flat probe which has a surface area greater than that of the sample. The compression is then maintained and the change in applied load as a function of time is recorded. The relaxation ability of the sample is calculated using equation (4.1) (Spearing, 2006):

$$Relaxation = \frac{F_{max} - F_{equilibrium}}{F_{max}} * 100 \tag{4.1}$$

Studies on gels have previously used cylindrical shaped gels for compression testing (Rogers, 2001). Therefore, as one of the wine gum shapes is cylindrical, approximately 12mm high with a diameter of approximately 22mm, this was used for compression testing. This did introduce some problems, for example many of the sweets were not perfectly cylindrical. The least deformed sweets were chosen in an effort to remove this problem. There is also raised lettering on the top of the wine gums which would affect the texture analysis. They were turned upside down and pressed on the reverse to minimise this effect but it could not be completely avoided. The chosen wine gums were placed one by one on the texture analyser. A 35mm cylindrical probe was used to compress the sweet to 40% deformation at 30mm/min and then it was held under this compression for 120 seconds.

The texture of wine gums changes considerably, even after packing. They are said to reach the optimum consumer texture 4 weeks after production. Consequently, if the method of producing conditioned wine gums were to be altered it would be necessary only to ensure that the same texture is seen after 4 weeks; it is not essential for the texture to be the same at the packing stage, providing they are firm enough to resist deformation. Therefore, several different batches of wine gums were tested 4 weeks after packing.

It was intended to take samples regularly throughout the year in order to take into account any seasonal changes in the texture which might occur. Four different batches were taken in April. It was intended to test other batches during the summer. However, wine gums were not being manufactured during the summer and the decision was then taken to change to sports mixture. One batch of sports mixture was tested.

4.2 Monitoring Conditioning

Conditioning is believed to solve three problems: stickiness, sweating and deformation. Therefore, wine gums were tested frequently during conditioning in different temperature and relative humidity environments to attempt to quantify these changes. These experiments were performed on two separate occasions using slightly different equipment. In both cases the wine gums were taken off the finishing line at the Sheffield factory but for the first experiment they were sent down to Bournville by courier to be tested (known from here on as the "Bournville tests"), whereas in the second case the experiments were done on site at Sheffield (the "Sheffield tests").

For the tests completed at Bournville, the exact time of finishing is not known but the wine gums are believed to have been approximately 4 hours old at the time of arrival. The batch was split into three and each was stored in a different temperature and humidity environment (dictated by the conditions of the available storage rooms at Bournville's Sensory Department). These conditions were: 20°C/ 45%RH, 25°C/ 45% RH and 25°C/ 75%RH. Another set of wine gums were stored in oil at 20°C to investigate the changes which occur in wine gums which are prevented from losing or gaining moisture. The wine gums were tested for stress relaxation and the force needed to separate two wine gums (to give a measure of stickiness) over a period of a week. They were also tested for moisture content, using the oven method, upon arrival and after 5 days. The tests done and the frequency of the tests were dictated by the situation in the laboratory at Bournville, for example it would have been preferable to test the moisture content using the Karl Fischer method, look at the change in mass over time as a non-destructive measure of change in moisture content and to test the moisture content more frequently. However, this was not possible.

Since the factory currently states that wine gums require a minimum of 12 hours to condition, it is clearly important to monitor the changes in texture, stickiness and moisture content within these first 12 hours, rather than considering wine gums which are already several hours old. This was the reason for performing the second trial in Sheffield and monitoring the wine gums immediately when they left the finishing line. Here there was access to just one storage cabinet so a range of conditions could not be tested simultaneously. Due to the limited time available at Sheffield, and since the behaviour in the later stages of conditioning was known for 20°C/ 45%RH (from the Bournville tests), it was decided to monitor wine gums at these conditions for just 24 hours. It was hoped that the two sets of data would then overlap to create a full description of conditioning in this environment from leaving the finishing line to a week old. However, after analysing this data it was clear that the data did not coincide with the Bournville tests and so it was decided to extend the monitoring period to 48 hours for the next the batch of wine gums that were tested.

The second batch was tested at 20°C/ 60% RH to investigate the effect of changing the relative humidity without changing the temperature. 60% was chosen since the current upper limit suggested by the factory is 55% therefore it was expected that this would demonstrate the detrimental effect of being above the 55% threshold on the product.

As with the Bournville tests, the Sheffield tests looked at the changes in stress relaxation and stickiness. However, it was also possible to look at the change in mass and ERH over time. The Karl Fischer method was used to look at local moisture contents but due to a problem with the equipment it could not be used to its full potential. Only a few samples were stored in petroleum gel and tested later to check if this was a viable method.

It was not possible to perform any further trials using Sheffield as a source

of wine gums due to the closure of the factory because of flooding. Producing wine gums in the pilot plant could have been used as an alternative source but this was also closed throughout the summer as a result of structural problems. Consequently, the data set in this section is incomplete.

The exact nature of each type of test is discussed below.

4.2.1 Sweating

As a preliminary check to establish the extent of sweating which would occur in non-conditioned confectionery, several batches of wine gums were bagged straight off the finishing line and stored. Every week a bag was selected to be opened so that it could be examined for signs of sweating.

4.2.2 Texture Analysis

The texture was analysed using the same technique which was used to characterise the texture. See section 4.1.1 for details.

4.2.3 Stickiness

The problems which have been experienced during packing have involved wine gums sticking together in clumps resulting in blockages of the packing machine. Therefore, in order to monitor the changes in the stickiness of wine gums during conditioning it seemed more appropriate to measure the force needed to separate two wine gums rather than using conventional texture analysis techniques which consider the adhesion of a sample to a probe. The method used was based on an approach used by Eeles and Groves (1995) to study conditioning and is shown schematically in Figure 4.1 on page 49.

The texture is analysed using a flat base and a large flat probe which has

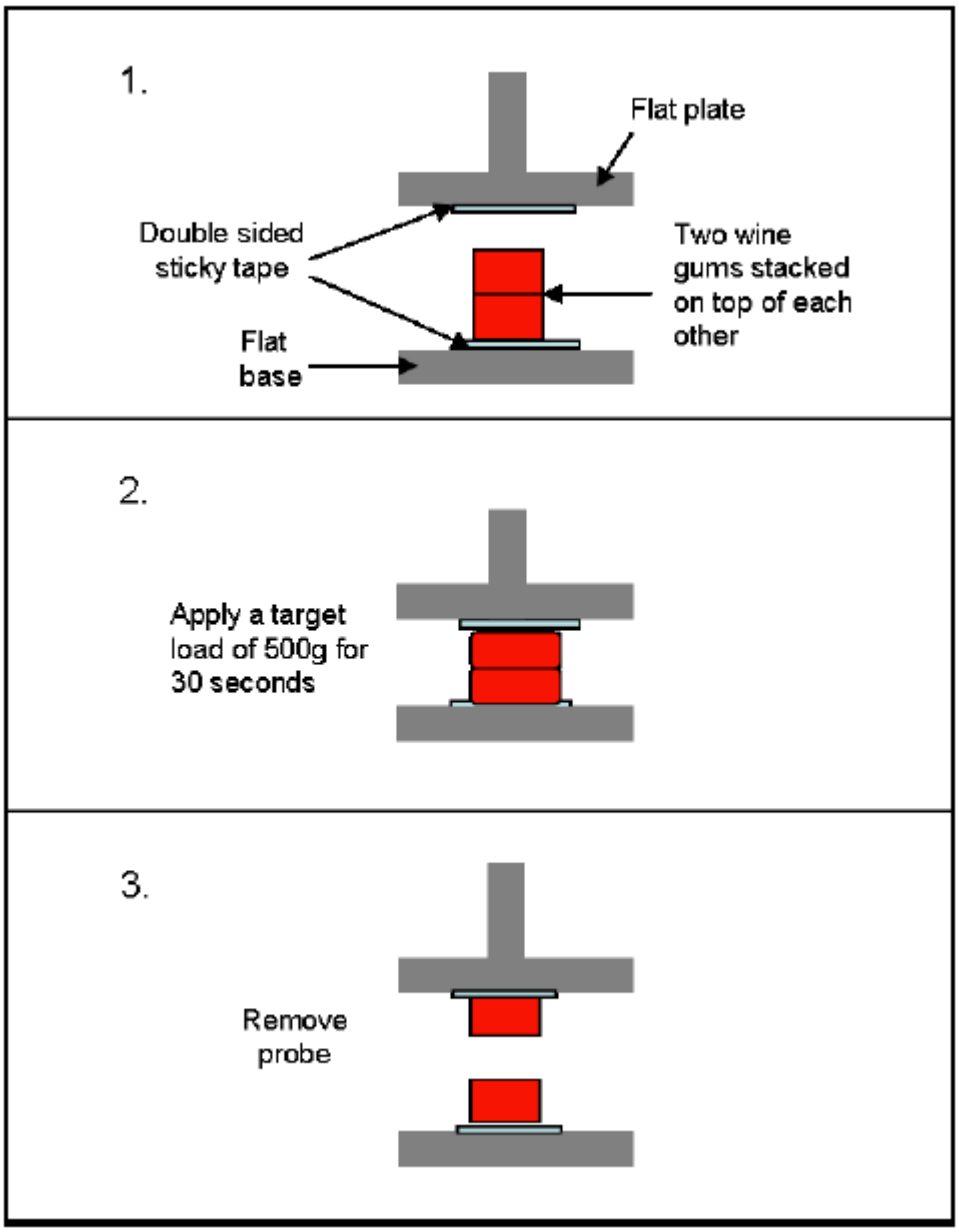

Figure 4.1: Schematic diagram illustrating the method for recording the force required to separate two wine gums.

a surface area greater than that of the wine gum. Double sided sticky tape is attached to both probes and then two wine gums are stacked onto the sticky tape on the base plate. The probe is lowered at a speed of 5mm/min until a target load of 500g has been reached. This load is held for a time period of 30 seconds before the probe is withdrawn. When the probe is withdrawn the upper wine gum remains attached to the probe and the lower wine gum remains attached to the base plate (because of the sticky tape) so the force which is measured by the texture analyser is that required to separate the two wine gums.

4.2.4 Moisture Content Analysis

4.2.4.1 The Oven Method

The oven method is a simple technique which allows the percentage moisture content in a sample to be calculated by completely dehydrating it and then calculating the loss in mass. As all the apparatus is thoroughly dried out in an oven and then cooled in a desiccator prior to use, all the mass which is lost can be attributed to the moisture originally present in the sample. The procedure is as follows: a flat bottomed metal dish containing around 25g of sand and a glass stirring rod is placed in an oven at 80°C and 25mBar, together with the lid to the dish, for one to two hours. This is then cooled in a desiccator for at least 45 minutes and accurately weighed. Approximately 5g of the wine gum sample is added to the dish and it is reweighed to determine the exact sample mass. $5cm^3$ of hot water is mixed in to disperse the wine gum and the mixture is placed over a boiling water bath for 20 -30 minutes to evaporate the excess water, stirring occasionally to ensure the contents are kept aerated. The dish is then removed from the water bath, the outside of the dish is thoroughly wiped to remove the moisture, and the dish, glass rod and lid (not fitted) are placed

in an 80°C (+/- 2°C) vacuum oven overnight (approximately 16 hours). After the required time the lid is replaced and the dish is cooled in a desiccator for at least 45 minutes. Finally, it is reweighed and the percentage moisture content calculated using equation (4.2):

$$\%moisture = change\,in\,mass/initial\,mass * 100 \tag{4.2}$$

4.2.4.2 Karl Fischer Moisture Content Analysis

The moisture content of a sample can be determined using a Karl Fischer titrator. This technique relies upon the chemical reaction between iodine, sulphur dioxide and water in an anhydrous medium containing methanol. This reaction may be represented by equation (4.3):

$$H_2O + I_2 + SO_2 + CH_3OH = 2HI + CH_3SO_4H \tag{4.3}$$

The water, present in the sample, and iodine, in the titrating reagent, are consumed in a 1:1 ratio. When all the water has reacted there will be an excess of iodine which will be detected electrometrically and which signals the end point. By using the known mass of the sample and the concentration and quantity of iodine used to reach the end point, the initial mass of water, and hence the percentage moisture content of the sample, can be calculated. In order to use this technique for gum based products such as wine gums, a 2:1 solution of methanol and formamide must be used, together with less than 0.1g of product. This is due to the relatively high moisture content which would affect the accuracy of the results if a higher mass was used. It is quite difficult to get such a small sample to be representative of the whole wine gum in order to calculate the average moisture content. A thin wedge is cut from the wine

gum to try to include the dry crust as well as the moist interior but there is some debate as to whether the results are actually representative of a whole wine gum. However, it will be a useful method for looking at local moisture contents. It is quite difficult to dissolve gum products so the titration must be done in a 50°C water bath and the sample must be homogenised for 200 seconds before the titration begins.

4.3 Differential Scanning Calorimetry

DSC is a thermo analytical technique which is used to investigate thermal events which occur during phase transitions. A sample pan and an empty reference pan with a known specific heat capacity are heated at the same rate and if any thermal events occur within the sample, for example melting or crystallisation, more or less energy needs to be added in order to keep heating at the same rate.

This technique was being used to rule out the possibility of starch retrogradation being responsible for the change in texture and expression of water thought to occur during conditioning. Although the presence of high levels of sugar and gelatine (both of which hinder retrogradation) make this scenario unlikely, it was thought worthwhile to run the tests to prove this conclusively.

Therefore, distilled water was added to the wine gum in the ratio of 4:1 in order to reduce the melting temperature of the amylose to below 100°C. The pans were then heated from 20°C to 100°C at 5°C per minute. The initial two tests were done using an approximate amount of water but these tests were repeated using a micro syringe to ensure a consistent quantity of water was added. The latter experiments caused the DSC pans to leak and almost ruined the machine. Consequently, this experiment was not repeated.

4.4 Dynamic Vapour Sorption

Dynamic vapour sorption (DVS) was used to calculate the diffusion coefficient of sports mixture for use in mathematical models. The DVS machine allows the change in mass of a microgram sample to be recorded over time when held at a particular temperature and relative humidity. A segment of sports mixture was removed from the centre of a sweet and placed in the DVS sample pan at 25°C / 45% RH for three days. The data obtained was then manipulated in order to calculate the diffusion coefficient using the initial gradient method described by Crank (1975).

4.5 X-Ray Tomography

An initial attempt at characterising the microstructure of wine gums was made using the technique of X-ray tomography. No evidence of similar successful studies were found in the literature but the technique is straightforward and quick. Approximately a 5mm diameter core was bored from the centre of a wine gum and inserted into the X-ray tomography machine. The sample was then X-rayed using a range of voltages and filters.

4.6 Light Microscopy

Light microscopy was also used to characterise the microstructure of confectionery, using both commercial sports mixture and sports mixture recipe deposited at high solid content (to remove the need for stoving) into plastic moulds.

Thin slices of the confectionery were cut using a knife then the specimens were placed on microscope slides and immersed in iodine solution, made up in

60% sucrose to minimise the risk of any sugars being washed out. They were then viewed under an Olympus microscope at a magnification of 500.

4.7 Transmission Electron Microscopy

This technique has been used successfully to study other confectionery products in the past, for example Ramesh Sukha et al (2002) cited TEM, along with dynamic mechanical thermal analysis (DMTA), as being the most useful techniques to characterise starch/ gelatine/ sugar gels as a function of the processing techniques and conditions. A study on wine gums performed by Elleman (2006) also successfully utilised TEM in order to study the microstructure as a function of processing.

Viewing a sample using TEM involves a long and complicated preparation, different depending on the type of sample to be studied. This is partly due to the size restriction of the samples to allow them to be partially electron transparent. This is limited by the mean free path of the electrons and so the sample must be sufficiently thin, usually less than 1 micrometre. This is usually only possible after embedding it into a solid medium which is strong enough to be sectioned this thinly. The sample must also be stained to increase the contrast in the sample, allowing different features to be distinguished. This is done by selectively depositing it in atoms which have a higher atomic number than those in the sample. The sample must be viewed in a vacuum to prevent electrons from scattering off the air molecules and this is a disadvantage as it means that samples must be dehydrated in either alcohol or methanol to remove any moisture. This could potentially damage the sample and cause, for example, shriveling. (Hayat, 1896)

In the case of wine gums, a standard biological treatment is employed. This involves fixing the sample with glutaraldehyde and osmium tetra oxide (OsO_4),

embedding in Epon epoxy resin and staining with uranyl acetate and lead citrate (Mercer, 1972). A similar procedure had been used on confectionery by Scuderi (2002) with successful results.

A green, cylindrical wine gum was chosen and samples were taken both from the edge and from the centre.

4.8 Determination of Phase Diagram

Gelatine / starch phase diagrams were determined at 3 different sugar concentrations: 0%wt , 5%wt and 30%wt. Stock solutions of 25%wt gelatine and 12%wt starch (with the appropriate concentrations of sugar) were made up at 95°C and then different amounts were added to vials to make up 25ml solutions of varying concentrations. 0.1% of Potassium Sorbate was added to each vial to prevent bacterial growth. The vials were mixed thoroughly for 2 minutes at 80°C and then left to equilibrate at 60°C (the temperature at which sports mixture are stoved). When equilibrium had been reached (taking more than a week in the high sugar, high gelatine cases) the vials were examined to determine whether the solutions had phase separated. A curve was fitted between the points at which phase separation did and did not happen as an approximation of the binodal.

Chapter 5

Results and Discussion

5.1 Characterisation of Texture

Four different batches of wine gums were tested for stress relaxation; the results are shown in the Table 5.1.

This gives an average relaxation of 63.71 with a standard deviation between batches of 5.62. Clearly there is a larger variation between different batches compared with the variation within a batch. The sports mixture yielded an average relaxation of 80.91 with a standard deviation of 1.83.

Relaxation	Standard Deviation
68.55	2.91
62.20	3.12
67.67	1.54
56.41	1.72

Table 5.1: Relaxation abilities and standard deviations of four batches of 4 week old wine gums

5.2 Monitoring Conditioning

5.2.1 Sweating

As a preliminary check to establish the extent of sweating which would occur in non-conditioned confectionery, several batches of wine gums were bagged straight off the finishing line and stored. Every week a bag was selected to be opened so that it could be examined for signs of sweating. There appeared to be no excess moisture either on any of the sweets or on the inside of the bag and therefore it has been concluded that conditioning is not necessary to prevent sweating and so this area of investigation will be discontinued. Although the checks were only done by sight and by feeling the inside of the bag and the sweets by hand, this was sufficient since it shows that if any moisture was exuded, the quantity was too low to be noticed by the consumer and hence not a problem.

5.2.2 Texture

The results of the Bournville and Sheffield tests are shown in Figure 5.1 and Figure 5.2 on page 58 respectively. The actual texture analyser used to obtain the results was different for each of the two tests, but it has been assumed that the results are comparable since the make and model of the texture analyser was the same in each case. However, this was not explicitly tested.

There is a difference of more than 20% between the initial relaxation value of the batch sent down to Bournville and the two batches sampled directly off the line. Of course the initial value of the Bournville sample is actually at least 4 hours old but the Sheffield batches did not reach this texture even after two days of conditioning so any aging which occurred during transport is unlikely to account for the difference. The impact this had on the way the samples

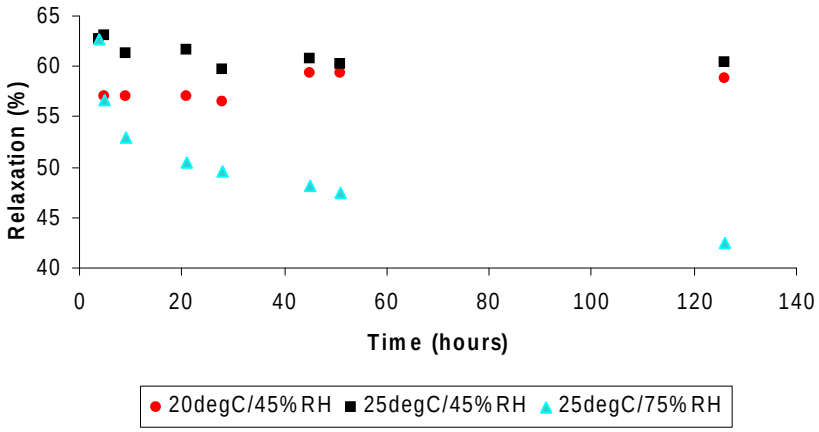

Figure 5.1: Change in texture over time for the Bournville batches, held at 20°C/ 45% RH, 25°C/ 45% RH and 25°C/ 75% RH

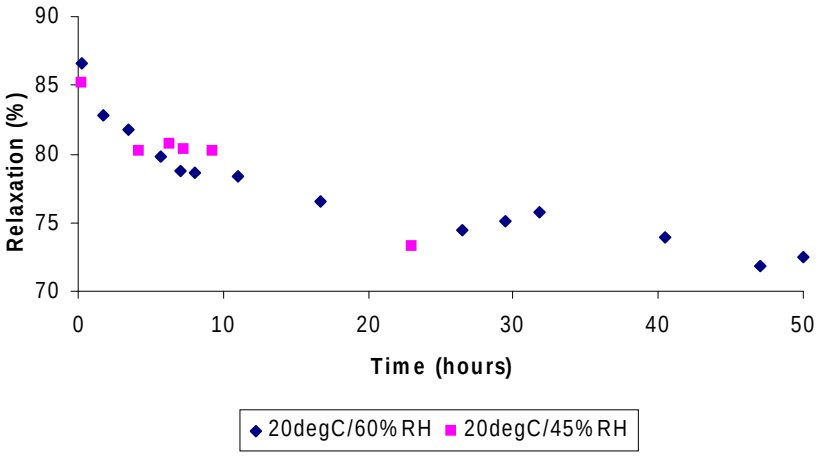

Figure 5.2: Change in texture over time for the Sheffield batches, held at 20°C/ 45% RH and 20°C/ 60% RH

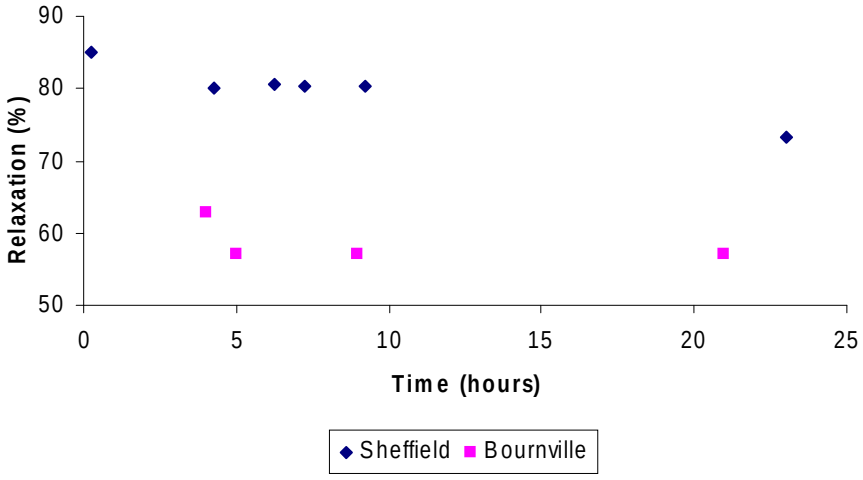

Figure 5.3: Change in texture over the first 24 hours of conditioning for the Bournville and Sheffield batches, both held at 20°C/ 45% RH

conditioned is evident by comparing the behaviour of the batches conditioned at 20°C/ 45%RH in the first 24 hours as shown in Figure 5.3 on page 59.

It is difficult to compare due to the missing few hours of the Bournville sample but there does seem to be some similarity. It appears that both have significant changes in texture in the first five hours and then the texture levels out. However, in the Sheffield sample the relaxation begins to decrease again after 10 hours whereas the Bournville sample remains constant. The Sheffield sample has a larger percentage change in texture over the 24 hours than the Bournville sample. Unfortunately, these Sheffield samples were not monitored after 24 hours so it is not known whether these samples would continue to change texture. However, the Bournville samples increased in relaxation slightly and then reached equilibrium within two days so it is possible that the values of texture would converge and eventually reach a similar value despite the large difference at the start.

The two Sheffield samples have very similar starting values and they followed

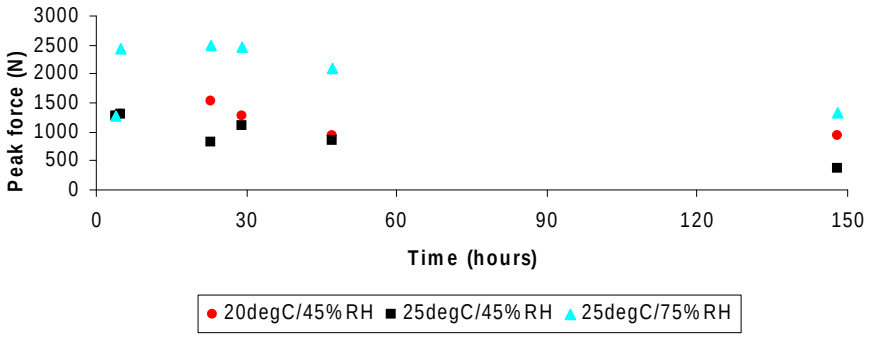

Figure 5.4: Change in stickiness over time for the Bournville batch at 20°C/ 45% RH, 25°C/ 45% RH and 20°C/ 75% RH

a very similar relaxation trend despite being at different conditions (see Figure Figure 5.2 on page 58).

5.2.3 Stickiness

The results from the texture analysis stickiness tests from the Bournville and Sheffield tests are shown in Figures 5.4 and 5.5 respectively.

It is difficult to draw conclusions from the stickiness data due to the large standard deviations in the results. However, there seems to be a large difference in the initial stickiness of all samples tested, covering a range of around 1500N over the 3 batches. This difference is far more significant than the subsequent changes in stickiness which occurred during conditioning. For example, although the stickiness of the 75% RH samples increased drastically during the first hour compared to the other samples, it still did not surpass the initial stickiness of one of the batches samples at Sheffield. At both conditions, the stickiness after 50 hours was not significantly different from the intitial stickiness.

Two possibilities for the initial differences in stickiness could be different

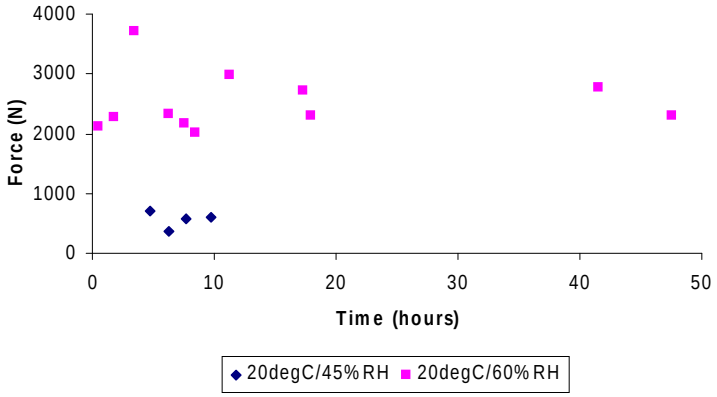

Figure 5.5: Change in stickiness over time for the Sheffield batch held at 20°C/ 45% RH and 20°C/ 60% RH

microstructures (see section 3.1.3.2) or different amounts of oil used for finishing. In a visit to Cadbury's Ernest Jackson factory during the summer, the Quality Control manager mentioned that they noticed packing problems when the sweets were either under- or over-oiled. This is rare because although they add oil to the drum at a specified rate, they recognise that every batch is slightly different and so the first few sweets of every batch are inspected after oiling and the dosing changed accordingly. This is in complete contrast to Sheffield where there is a set dosage and this is never changed. Also, the length of time spent in the drum is not well controlled and has been gradually reducing over the last few years so it is debatable whether a satisfactory standard of oiling is still being achieved. The wine gums leave the oiling drum with a speckled coating of oil, rather than being uniformly coated as the sweets at Ernest Jackson are. This oil appears to gradually redistribute itself over the course of conditioning. However, before it has chance to do this there is a reduced barrier to moisture and (assuming a lack of oil increases stickiness) an opportunity for the units to stick together. Therefore, ensuring that sweets are fully coated with the optimal quantity of oil could be vital. (The Engineering staff at Sheffield have now put oiling on

Condition	Change in Mass (%)
20°C, 45%RH	-1.3
25°C, 45%RH	-2.3
25°C, 75%RH	+2.5

Table 5.2: Average percentage change in mass of wine gums conditioned for a week at 20°C/ 45%RH, 25°C/ 45%RH and 25°C/ 75%RH

a list of problems which need to be addressed so they do recognise that this is an issue). Both oiling and phase separation need to be investigated in the near future to see the impact on the levels of stickiness.

5.2.4 Moisture Content

Due to problems with moisture content analysis at the time of testing during the Sheffield tests, changes in mass were used as a measure of water loss or gain. Whilst it is reasonable to assume changes in mass are exclusively due to moisture loss/gain, it does not necessarily follow that differences in initial masses are due to moisture content differences. For the Sheffield samples, the difference between the initial masses was much greater than the loss or gain in mass which occurred as a result of conditioning and yet there was not a large difference in the initial texture.

As expected, wine gums stored below the ERH lost moisture and those stored above gained moisture, with the exact amount being proportional to the modulus of the difference and the temperature. Table 5.2 shows the average amount of moisture lost or gained after a week of conditioning. A control sample of wine gums were stored in oil did not change mass over the week.

These results suggest that the samples stored at 25°C lost or gained moisture at a significantly faster rate than those at 20°C, emphasising the temperature dependence of the diffusion coefficient. In fact, keeping the relative humidity constant but increasing the temperature by 5°C caused double the amount of

moisture to be lost (0.12g compared to 0.06g). At a constant temperature but different relative humidities the percentage moisture content of the samples changed by a similar amount, although one sample lost moisture and the other gained because one condition was above the ERH and the other was below. A greater range of conditions would need to be tested to see if these conclusions apply to other temperature and relative humidity conditions.

It is not possible to compare the moisture loss between wine gums which were different in initial moisture content but held at the same conditions because, by coincidence, the Bournville samples (some of which were held at 20°C/45% RH) and the Sheffield samples which were held at 20°C/45% RH had almost identical moisture contents (17.9% and 17.87% respectively). They were then seen to lose similar amounts of moisture, on average, per day (0.13% and 0.11% respectively) as expected.

During the Sheffield experiments the Karl Fischer apparatus was not working properly. However, in order to test the method of looking at local moisture contents, samples were removed from the edges and centres of wine gums and stored in petroleum jelly until later testing could be done. The moisture content was then tested and the difference in moisture content between the edge and the centre of each wine gum was examined.

The results, displayed in Figure 5.6, strongly suggest that a moisture gradient does exist in the sweet from the centre to the edge with the centre at a moisture content of around 4% above that at the edge. The moisture then begins to redistribute over time, moving towards a state of equilibrium throughout the sweet. Whether this distribution has any impact on conditioning cannot be seen from these results, although if a similar pattern was seen after testing a range of wine gums at each time interval rather than one, it would imply that the moisture equilibrates more quickly at 45% RH (at least over the first 24 hours).

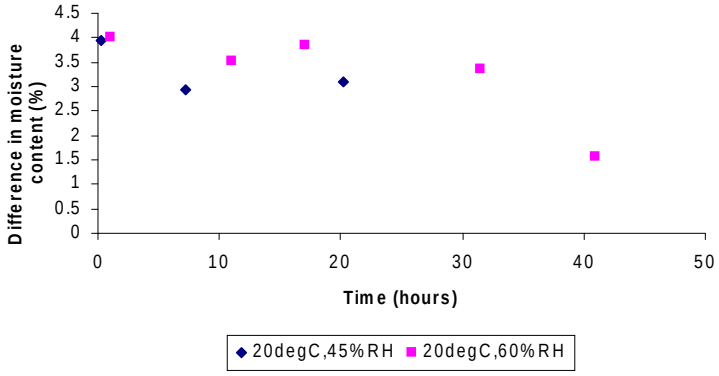

Figure 5.6: Difference in percentage moisture content between the centre amd the edge of a wine gum held at 20°C/ 45% RH and 20°C/ 60% RH

Since no difference in texture was seen between the two samples over this time period it could suggest that attaining equilibrium does not affect the texture.

Although the results seem promising only one wine gum was tested at each time and therefore the results are not as useful as they could be. In order to obtain valid results which show a trend over time a number of wine gums need to be evaluated at regular time intervals and an average value obtained.

5.2.4.1 ERH

The ERH of the samples conditioned at both moisture contents increased over time, as shown in Figure 5.7. Although not many measurements were taken for the samples stored at 45% RH, it seems as though there was an initial difference in the ERH between the two batches but then the ERH of both samples increased at a broadly similar rate. This supports the Karl Fischer data above which suggests that the moisture content of the edge increases because the ERH data only relates to the edge of the wine gum and an increasing ERH

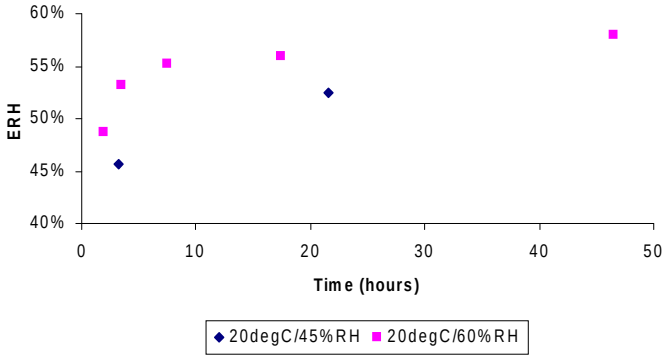

Figure 5.7: Change in ERH over time at 20°C/ 45% RH and 20°C/ 60% RH

implies an increasing moisture content.

5.2.5 Changes during Conditioning

The general trend seems to be for the relaxation to decrease over time which implies the samples are becoming more elastic and resisting deformation to a greater extent. This is as expected and agrees with what is physically observed. The decrease does not occur at a constant rate but tends to drop and plateau intermittently (Figure 5.1 and Figure 5.2 on page 58).

There seems to be a small decrease in stickiness over time for the Bournville samples (up to 500N), particularly those held at 25°C, but the Sheffield samples did not appear to significantly change in stickiness over the time period considered (Figures 5.4 and 5.5).

A change in moisture content was seen in all samples with the magnitude of the change being dependent on the external conditions.

5.2.6 Conditioning and Batch Variation

A commonly held belief in the factory is that the variability of the conditions

in the conditioning area have a large, and negative, effect on the consistency of the product. For example, the characterisation texture results in Chapter 5 provide some indication of how variable wine gums from different bags are. However, the results above show that the products vary even before they reach the conditioning areas.

5.2.7 Conditioning process and External Conditions

The conditions in the conditioning areas are known to vary widely so it was important to consider how much this impacted on the product. Surprisingly, it was not found to be as important as first thought for the conditions tested. However, due to the problems mentioned in the Methods section only a limited range of conditions were tested so more conditions would need to be tested before a valid conclusion can be reached.

5.2.7.1 Texture

All the batches tested did not reach the same texture over the time periods tested (but this time scale was relatively short for the Sheffield samples). This is not surprising due to the large initial differences in the samples. However, the samples which started at comparable textures did end up at similar textures. The exception to this was the 25°C/ 75% RH sample which continued to decrease in relaxation throughout the week, whereas the other samples reached a plateau, and therefore ended up at a much lower value. The difference between this sample and the others was also apparent when eating the samples; the 25°C/ 75% RH sample was quite unpleasant after only a few hours.

The 25°C/ 45% RH sample reached a constant value most quickly, appearing to stabilise after 24 hours. The 20°C/ 45% RH sample took around 44 hours to stabilise. The differences in the two Bournville samples held at 45%RH may

have been within experimental error. The experiment would need to be repeated before it can conclusively be stated that the 25°C samples reached equilibrium before the 20°C sample. The Sheffield samples did not reach an equilibrium value over the 48 hours tested.

It was expected that the samples should reach equilibrium within a week since this is the maximum time allowed for conditioning and so it should be assumed that the sweets are conditioned within this time. This suggests that for the Bournville batch a relaxation value of 60 represents an effectively conditioned wine gum and that the higher temperature conditions were more favourable in terms of reaching this point in the lowest possible time. This could be due to increased temperature increasing the rate of moisture movement within the sweet, thereby allowing the moisture to equilibrate more quickly.

5.2.7.2 Stickiness

The 75%RH sample increased in stickiness significantly after an hour in the cabinet but then gradually decreased in stickiness. After a week they were still stickier than they were initially. The other two Bournville samples appeared to decrease in stickiness throughout the week but the Sheffield samples did not change stickiness, even the sample stored at 60%RH. This was surprising since the factory imposes a relative humidity limit of 55% because it is believed that sweets become excessively sticky when stored above this.

The results above suggest that wine gums are not as sensitive to the relative humidity as previously thought. Clearly, a limit must be imposed since the 75% sample became much stickier after just an hour, but this limit could be higher than 60%.

The fluctuations in the recorded average force for the Sheffield samples were much greater than for the Bournville samples. For example, the sweets in the

60% cabinet did appear to dramatically increase in stickiness in the first few hours but at the end of two days the stickiness was not significantly different from at the start. Any small peaks and troughs in the data cannot really be seen as significant due to the large variability in the values obtained.

The stickiness data was not as reliable as the stress relaxation data and had large standard deviations. As a result, although the 25°C/ 75% RH sample was clearly stickier than the other two (this sample could be picked out by touch alone), the difference between the 20°C sample and the 25°C sample (both stored at 45% RH) could not be considered significant. The method for stickiness testing needs to be modified in order to increase the accuracy of the tests, but this method was sufficient to show the detrimental effect of storing samples at such elevated relative humidity values. Again this emphasises why RH limits have been specified for the factory conditioning areas, and why theses limits should be adhered to (although this is not always possible).

5.2.7.3 Change in Mass

Excessive moisture loss or gain cannot be considered to be beneficial when conditioning; although wine gums have a large acceptable range of moisture contents, changing moisture content at the rates seen in the 25°C samples would result in a sweet which was initially in the middle of the acceptable range being outside it within a few days (for example, this was the case for the Bournville samples conditioned at 75%RH). Since sweets can be left in the conditioning area for up to a week this would result in significant loss of product.

As well as affecting eating quality, the moisture content affects the recipe percentages and hence the nutritional content of the product per 100g. Therefore, achieving a consistent moisture content is important to ensure that the nutritional information displayed on the packet is accurate. Excessive moisture

gain or loss would compromise this accuracy.

5.2.8 Relationship between Moisture Content and Texture

The Bournville samples and the Sheffield 20°C/45%RH samples both had the same initial moisture contents and yet their values of relaxation differed by more than 20%. They proceeded to lose similar amounts of moisture per day and yet the relaxation of the Sheffield sample reduced by a greater amount than the Bournville sample.

During the trials at Bournville a selection of wine gums were stored in oil for the duration of the experiment so that the sample could not gain or lose moisture. Therefore, the moisture content was the same as when the sweets first arrived, and yet the texture was considerably different, with a value in between that of the 45% RH sample and the 75% RH sample after 5 days. The moisture within these sweets appeared to have equilibrated, and there was no evidence of a dry crust present on the outside. These sweets were also of inferior eating quality suggesting that attaining a state of perfectly uniform moisture is not the aim of conditioning; a dry crust must still exist to some extent in a consumer ready wine gum.

In the Sheffield trials, despite the fact that one sample gained moisture whilst the other lost moisture, the textural behaviour appeared to be very similar over the timescales which were considered.

Altogether these observations provide strong evidence that moisture loss or gain is not responsible for the change in texture seen during conditioning.

Of course there is a relationship between moisture content and texture; this is well known and is one of the reasons that target moisture content is the main criteria used when altering manufacturing processes (as well as the impact

on labeling). However, there are clearly other factors which also affect the texture. In addition to this, the changes in moisture content which occur during conditioning are generally small and not likely to significantly affect the texture. One exception to this is the sample held at 75% RH; this caused such a large increase in moisture that the total moisture content ended up far outside the acceptable range. Changes of this magnitude are likely to affect the texture and also the eating quality (these wine gums were noticeably unpleasant after just a few hours). In fact, these wine gums changed in character to such an extent that they would not be allowed to be packaged and so these results should not be taken to describe a conditioned wine gum.

5.2.9 Effect of Gelatine

In the literature review it was suggested that the increase in firmness of the wine gums during conditioning could either be as a result of increasing gel strength or as a result of moisture redistribution. Trying to separate the effects of these two processes was quite difficult since a wine gum which has just been finished has a dry crust and a moist centre. Therefore, even if it is submerged in oil to prevent any moisture loss, the moisture will still be redistributing within the wine gum and hence any hardening effects cannot be attributed exclusively to the build up of the gelatine gel network. To avoid this, a cube of approximately $2mm^3$ was removed from the centre of the wine gum, small enough to ensure that the moisture throughout the cube was uniform. Texture profile analysis was performed on cubes which had just been removed. Others were stored in oil to prevent moisture loss whilst others were left within the wine gum and only removed immediately before testing. All the samples were left for two days to allow sufficient time for the gelatine network to develop, or for the moisture to redistribute, as in the case of the cubes left in the wine

gums.

If the samples in oil became harder this would be as a result of the increase in gelatine. If the samples within the wine gum became harder by the same amount as those in oil then this would suggest that the movement of moisture did not contribute to the hardness, whereas if they were significantly harder than those in oil it would demonstrate the effect of the moisture.

Unfortunately, the texture analyser gives notoriously variable results anyway, and in this case the errors were magnified by the base effects due to the small samples. It was very difficult to cut evenly sized cubes, particularly from the unconditioned wine gums which were very soft and sticky inside. As a result of all these issues the hardness values were too variable to be significant and no correlation was found.

An alternative method was then attempted. As the key issue is to have samples which are uniform in moisture content, unstoved sports mixture was deposited at final solids into plastic moulds. They were covered to prevent moisture loss and then stored for 3 hours at 20°C to allow gelation (this is the standard cooling cycle for Sports Mixture once they have reached their target moisture content during starch moulding). The intention was to monitor the relaxation over a period of several days whilst the Sports Mixture was stored in the moulds to prevent any moisture loss. The fact that they were deposited with a uniform moisture profile would remove the possibility of moisture movement within the unit and therefore any increase in hardness would be as a result of a build up of the gelatine network.

Because the Sports Mixture had not been stoved the exterior was extremely sticky therefore it was considerably difficult to extract the sweets from the moulds. As a result, some of the outsides were damaged so it was decided to remove cuboids from the centre, roughly $2cm^2$ by 1cm. They were then

Time after depositing (hrs)	Moisture Content (%)
5	
29	16.9
53	16.4
77	16.2

Table 5.3: Change in moisture content over time of the final solids Sports Mixture, stored in plastic moulds to minimise moisture loss

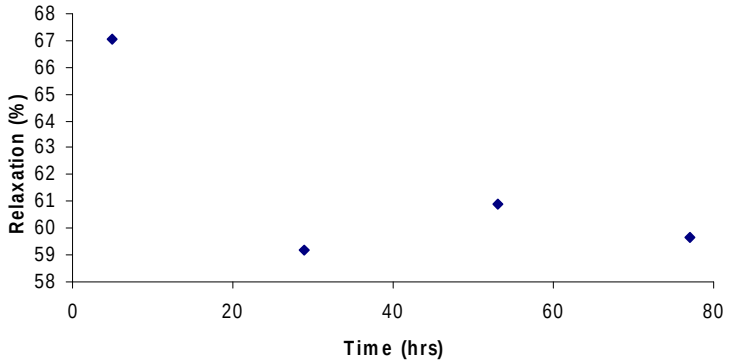

Figure 5.8: Change in texture over time of the final solids Sports Mixture

wrapped in cling film (to prevent damage to the texture analyser) and tested using stress relaxation. The results were not as consistent as those obtained using finished sweets, probably due to the difficulty in obtaining consistent sized units because of the stickiness.

The results are presented in Table 5.3 and Figure 5.8.

Unfortunately, the samples were not able to be tested for moisture after depositing so the initial moisture cannot be known. The moisture content analysis was performed to ensure that the samples were not losing moisture but this clearly was not the case from hour 29 to hour 77, over which a loss of 0.7% moisture was recorded. However, this change in moisture was not sufficient to affect the texture of the samples. Since the initial moisture content is unknown a firm conclusion cannot be drawn as to whether the initial drop in relaxation

was due to moisture loss or due to other factors.

Overall, the trend of relaxation i.e. dropping significantly in the first 24 hours and then remaining relatively constant afterwards appears to be very similar to the trend seen in conditioning gums. This experiment needs to be modified to ensure that no moisture loss occurs, for example by storing the samples in oil, and the frequency of the texture analysis needs to be increased, particularly in the first 48 hours. If it then yields similar results to conditioning sweets (made in the same batch but deposited at normal solid content and stoved), it would provide compelling evidence that moisture movement is not the main purpose of conditioning as has been commonly believed.

5.3 Differential Scanning Calorimetry

Two samples of Sports Mixture were tested using Differential Scanning Calorimetry. More samples were not tested because due to a badly designed method the DSC pans leaked, almost resulting in destruction of the calorimeter. The two traces which were obtained are shown in Figure 5.9 and Figure 5.10.

The figures show the energy which needed to be supplied to a mixture of distilled water and Sports Mixture in order to heat it at the same rate as an empty DSC pan. The peaks of the two traces do not coincide in terms of temperature or enthalpy. It is felt that this may be due to the inconsistent quantities of water which were added.

In Figure 5.9 there appears to be two melting peaks, one at 80°C and the other at 100°C. The latter peak is likely to be the latent heat associated with evaporating the water. The former is possibly the solid sports mixture structure melting, leaving the liquid state which has a higher specific heat capacity (seen by the step in the heat flow). There are no crystalline melting peaks (which due to the labeling convention on the graph would appear as troughs in the

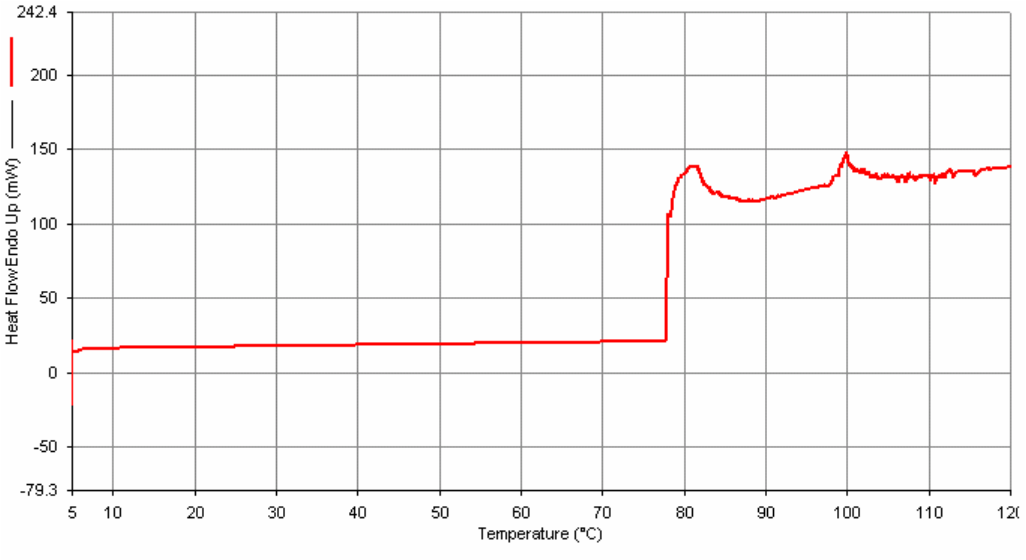

Figure 5.9: Energy needed to heat a sample of sports mixture and water at the same rate as an empty DSC pan - trial 1

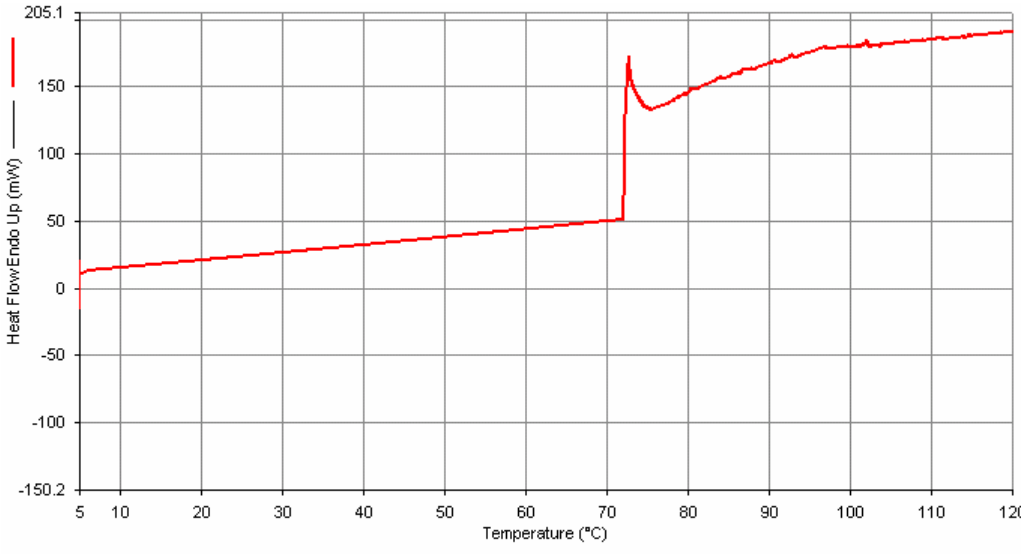

Figure 5.10: Energy needed to heat a sample of sports mixture and water at the same rate as an empty DSC pan - trial 2

graph rather than peaks) suggesting that retrogradation has not occurred. If the amylopectin in the starch had recrystallised this crystal structure would have melted as the wine gum was heated, leading to a trough in the graph at around 55 - 65°C.

The evaporation peak at 100°C is not so evident in Figure 5.10 and the melting peak is at a slightly lower temperature, approximately 72°C. The heat capacities both before and after melting continue to rise rather than remaining constant as it did in the first trace.

The data was used to calculate values of the specific heat capacity, c, using the equation Q = mc$\triangle$T , where Q is the amount of energy in Joules needed to raise m kilograms of a material through a temperature change of $\triangle$T Kelvin. However, since the mass of the sports mixture and water was 13.24mg, the heating rate was 0.05Ks^{-1}and the power required was 20mW, this leads to the following calculation: c = Q mT = $20\times10^{-3}\times13.24\times10^{-6}\times$ 0.05 = 30.21kJkg^{-1}K^{-1} which gives a highly unrealistic value which is around 2 orders of magnitude higher than would be expected for a solid. Similarly, the value of the liquid phase was unrealistic at 181.3kJkg^{-1}K^{-1}. A particularly low heating rate was used in order to identify any thermal events but accurate calculation of specific heat capacity requires high heating rates. However, it seems unlikely that this would lead to such large errors.

5.4 Dynamic Vapour Sorption

The drying curve obtained using DVS is shown in Figure 5.11.

As described by Crank, the diffusion coefficient of a sample can be approximated using equation (5.1).

$$\frac{m_t}{m} = 2\frac{S}{V}\left(\frac{D}{\pi}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \tag{5.1}$$

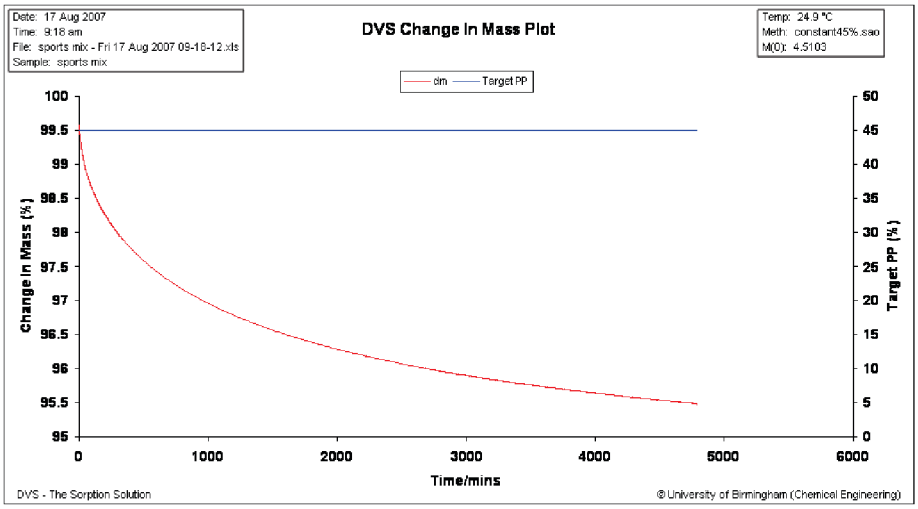

Figure 5.11: The drying curve of a wine gum obtained using Dynamic Vapour Sorption

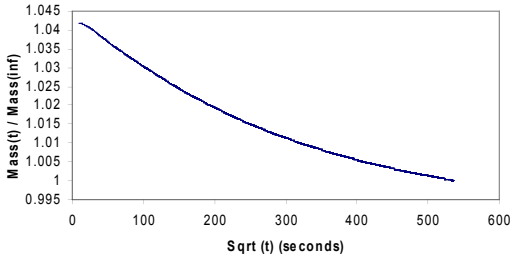

Figure 5.12: Graph used to calculate the diffusion coefficient

where m_t is the mass at time t, m is the mass after an infinite time, S is the surface area of the sample, V is the volume of the sample, D is the diffusion coefficient, and t is the time. Therefore, the diffusion coefficient can be found be plotting $\frac{m_t}{m_\infty}$ against $t^{\frac{1}{2}}$, equating the gradient to $2\frac{S}{V}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}$ and rearranging for D. This graph is shown in Figure 5.12.

This yields a diffusion coefficient of $3.14 \times 10^{-10}\mathrm{m}^2\mathrm{s}^{-1}$. Due to a restriction on the length of time the DVS machine is available for booking, coupled with the high moisture content of sports mixture, the mass of the sample did not

reach equilibrium during the experiment. Consequently, a reasonable estimate of the mass after an infinite time period could not be obtained. An attempt was made to fit an exponential curve to the data in order to predict a more realistic value but the data clearly was not exponential so a curve could not be fitted and the mass value at the end point of the experiment had to be used. This makes the final value of the diffusion coefficient inaccurate. However, it is of the same order of magnitude as the value of the moisture diffusion coefficient in confectionery found by Sudharsan et al. ($1.7 \times 10^{-10} m^2 s^{-1}$).

5.5 X-Ray Tomography

Due to the similarity in density of the starch and gelatine components no useful information could be gained from this technique as shown in Figure 5.13.

5.6 Light Microscopy

Micrographs were taken of sports mixture sweets in order to identify the microstructure. An example is shown in Figure 5.14. The staining method used did not produce images of sufficient clarity to allow any quantitative analysis to be performed. In all the micrographs the more darkly stained regions are starch whereas the bright unstained regions are gelatine.

Similar micrographs were taken of a gel made from sports mixture recipe but deposited into a plastic mould and simply left to set for 3 hours at 20°C rather than being stoved at 60°C for 3 days and then cooled at 20°C for 3 hours as commercial sports mixture would be. An example is shown in Figure 5.15.

Despite having identical recipes, the two products have extremely different

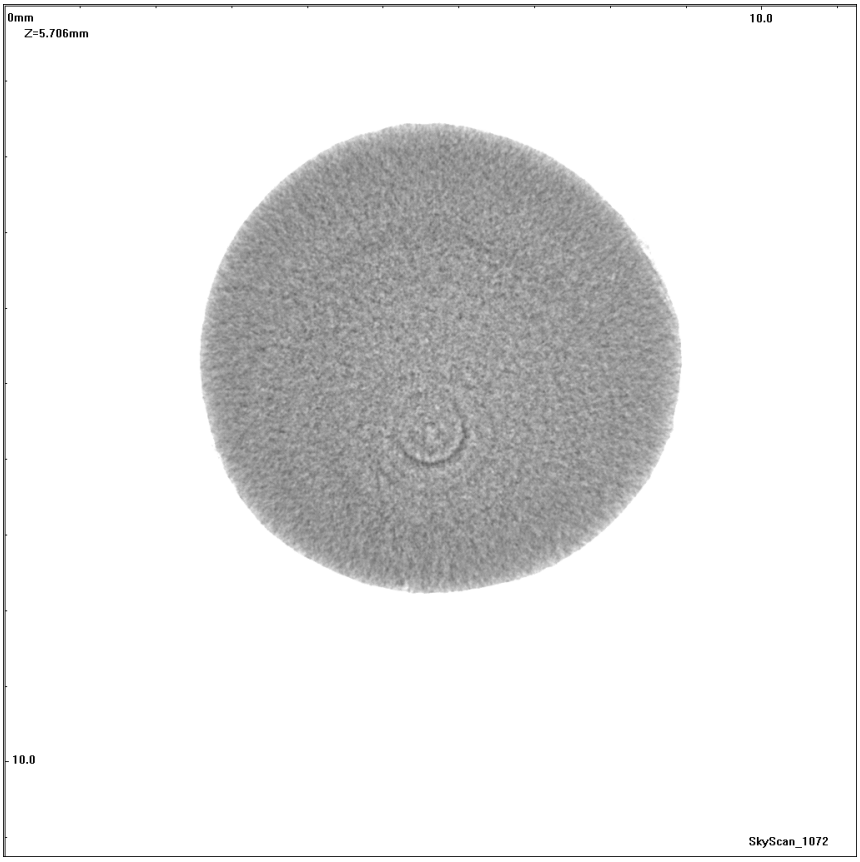

Figure 5.13: The image obtained using X-ray tomography on a wine gum

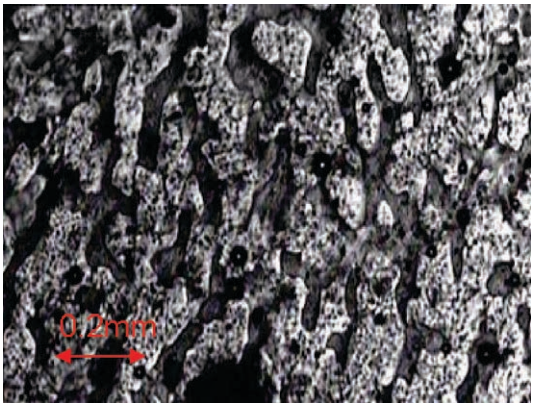

Figure 5.14: Micrograph of the sports mixture sample

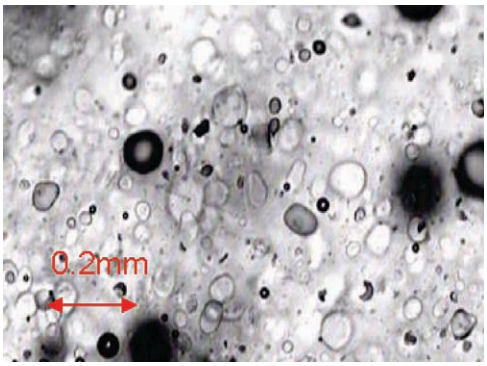

Figure 5.15: Micrograph from the final solids gel

microstructures. This is as a result of the differences in processing. The commercial product has a bicontinuous structure with secondary phase separation occurring, particularly in the gelatine phase. Conversely, the final solids product has a droplet morphology with gelatine as the discontinuous phase. These concur with the results described in the phase separation literature review. A fast cooling rate where the phase separation is competing with gelation, as in the case of the final solids mixture which was quenched from around 100°C directly down to 20°C, gives rise to small inclusions of the discontinuous phase, whereas holding the mixture above the gelation temperature (as in the case of commercial sports mixture, held at 60°C) leads to larger inclusions. Although the mixture was left to phase separate for more than 3 days a percolation to cluster transition did not occur and the microstructure remained bicontinuous. This may be because the concentrations of starch and gelatine are at the critical concentration; Loren suggests that a mixture quenched at the critical concentration remains bicontinuous rather than under going a percolation to cluster transition, even at later stages of spinodal decomposition. The sports mixture was drying throughout the holding period at 60°C. This would have led to two competing processes: the solution would be becoming more concentrated which would drive the phase transition but the decrease in moisture content would

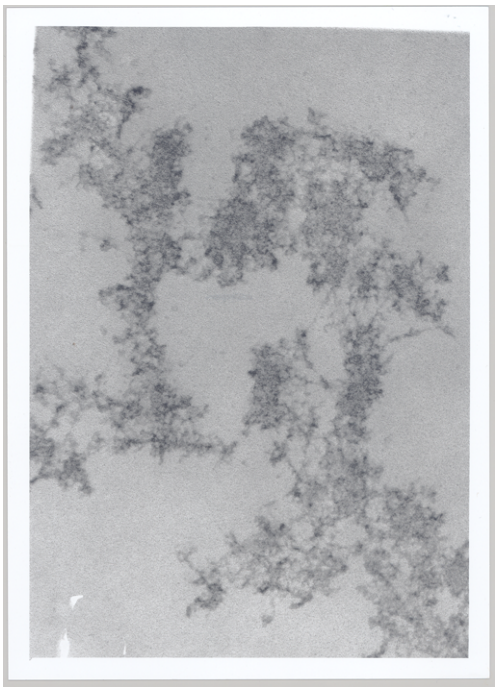

Figure 5.16: Micrograph of the edge sample of wine gum

increase the viscosity of the solution, preventing the mobility of the polymers and hindering the phase separation. This manifest itself as secondary phase separation with the thermodynamic incompatibility causing the phases to try to separate, even within a phase which has already become highly concentrated in one polymer, but the high viscosity preventing the demixed starch from migrating to the starch rich phase.

5.7 Transmission Electron Microscopy

Micrographs were taken at the same magnification for both samples to allow direct comparison, as seen in Figures 5.16 and 5.17. Although the procedure used to prepare the samples was extremely similar to the methodology used by Scuderi, with just a few minor differences based on the recommendations of the

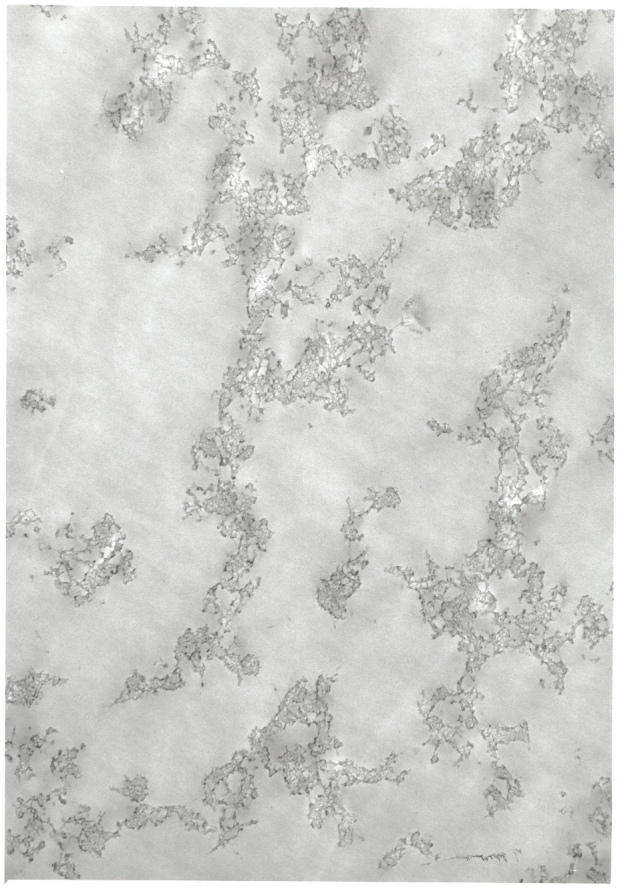

Figure 5.17: Micrograph of centre sample of wine gum

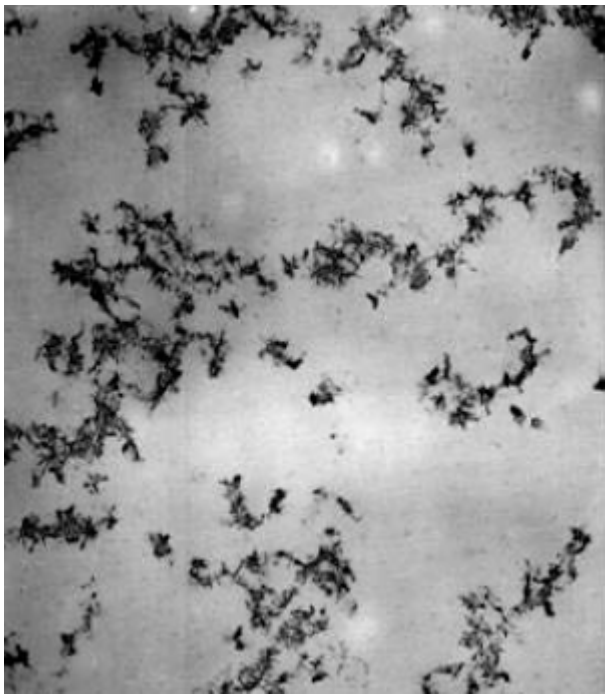

Figure 5.18: Pure starch sample at a magnification of 20k. (Scuderi, 2002).

staff at the Electron Microscopy Centre, the micrographs obtained did not look as expected when compared to Figure 3.2 on page 21. It was then realised that these micrographs look extremely similar to the micrographs Scuderi obtained of close ups of pure carbohydrate samples, as shown in Figure 5.18 (Scuderi, 2002). This convincingly shows that the TEM micrographs obtained simply show carbohydrate. This could either be because the gelatine was not stained correctly, or because due to the restricted field of view, only the starch phase was seen. The latter explanation is unlikely since samples were examined from both crust and centre and all looked identical.

There appear to be a small number of starch granules present. An example is shown in Figure 5.19. There were also other electron dense regions which

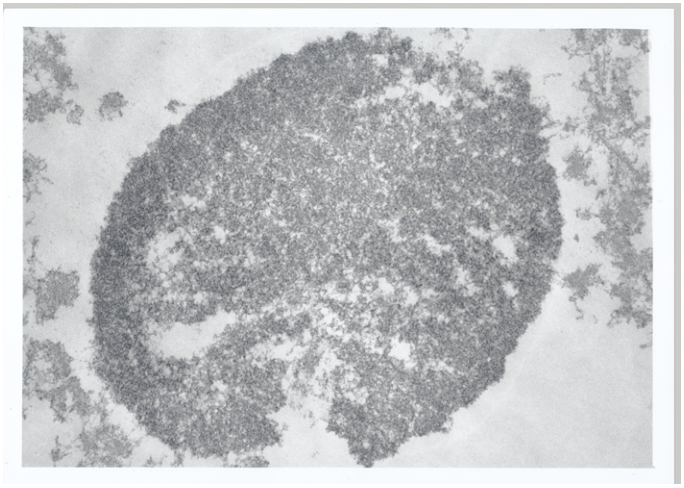

Figure 5.19: Micrograph of an electron dense region from the edge sample at a magnification of 20k, thought to be a starch granule.

were possibly parts of ruptured granules, as shown in Figure 5.20.

A large difference was seen in the samples during processing; the centre samples did not stain as darkly as expected and appeared to break up quite significantly. However, the cause of this was unknown and the micrographs of the edge and centre did not show significant differences from each other which would account for this.

The fact that the gelatine did not stain is likely to be as a result of the preparation used. Although the method was based on that used by Scuderi, his procedures were not thoroughly documented and hence a fundamental step may have been omitted.

Further examination of the micrographs produced by Scuderi and Elleman reveals bright patches around the edges of the discrete phases. This is thought to be as a result of the different phases shrinking by different amounts during the dehydration process, leaving gaps between the phases which were not previously present. Therefore, despite the sources citing TEM as a useful technique for this type of confectionery it seems that the stressful preparatory procedures do have

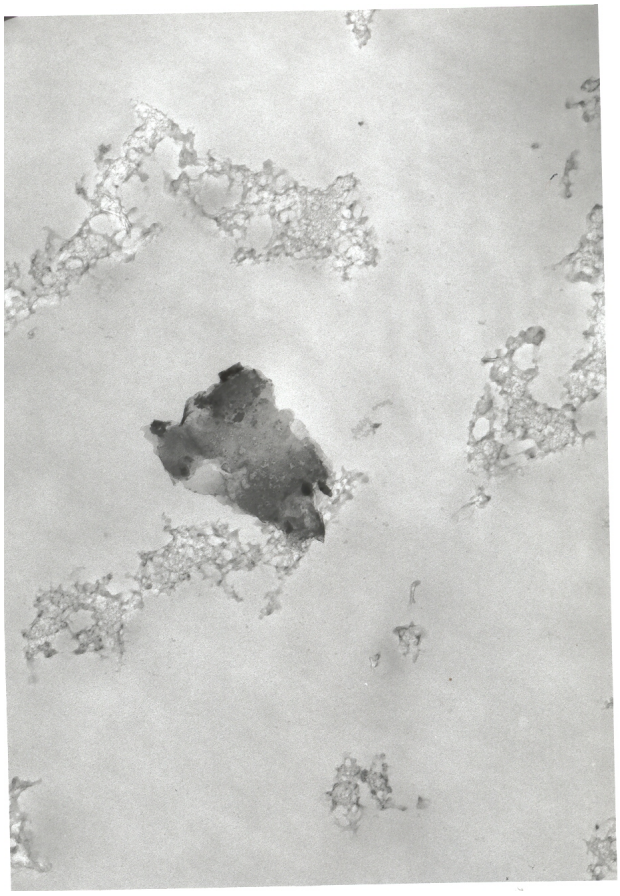

Figure 5.20: Micrograph of an electron dense region from the centre sample at a magnification of 20k, likely to be a fragment of a starch granule.

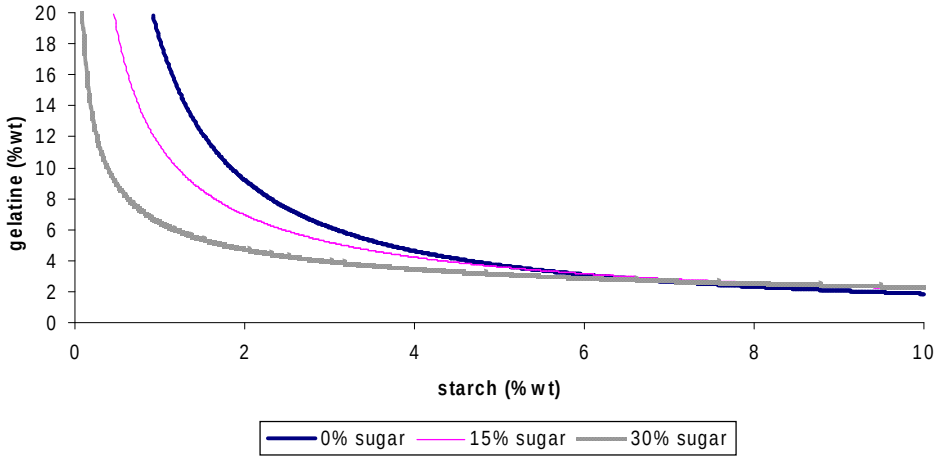

Figure 5.21: Phase diagram of gelatine and starch at 0% sugar, 15% sugar and 30% sugar

quite an effect on the results.

5.8 Determination of Phase Diagram

The phase diagrams for 0%, 15% and 30% sugar are shown in Figure 5.21. The curves represent the binodals of the curves so the areas above the binodals are the phase separated regions and the areas below are the single phase regions. The curve representing the 0% sugar case has the largest area beneath the curve, implying that water is the best solvent out of those tested, promoting miscibility more effectively than the sugar solutions. The more sugar that was added the more poor the solvent became.

Chapter 6

Conclusions

Characterisation

The texture of consumer ready (i.e. four week old) wine gums and sports mixture needed to be characterised so that if any changes are made to the conditioning process it could be ensured that no change was made to the texture. The collection of this data was started but should be continued, particularly at varying times of the year, so that seasonal variations are taken into account. Although the textural results were in general extremely variable, the relaxation of the batch was quite consistent and so could be used when developing the control texture. The initial data also suggested that the variation between batches was more significant than variation within batches. This variation could potentially be beneficial if the manufacturing process is changed since it will be easier to match the texture if there is a broader acceptable range.

Performing Differential Scanning Calorimetry on sports mixture mixed with distilled water (with a water / sports mixture ratio of ≥ 3) showed an endothermic peak at 70 - 80°C, probably the solid sports mixture structure melting, and

another at 100°C as the water evaporates. There was an increase in specific heat capacity when the sweet changed from solid to liquid form but the actual values were not calculated properly, possibly due to the low heating rate or calculational error.

DVS was attempted numerous times but due to the high moisture content of the confectionery the time required for the sample to reach equilibrium at a given relative humidity was longer than the maximum time allowed on the machine. This meant that the mass after an infinite time was not determined and hence the validity of the calculated diffusion coefficient is questionable. However, at 45% RH, the value of the diffusion coefficient was calculated as $3.14\times\ 10^{-10}\mathrm{m}^2\mathrm{s}^{-1}$.

In terms of characterising the microstructure, both X-ray tomography and TEM were found to be unsuitable. For the X-ray tomography, this was due to the similarity in density of the starch and gelatine phases. For TEM it was due to the staining method used, only allowing the starch phase to be seen. Although a different staining technique could be attempted, TEM is time consuming and expensive and light microscopy was seen to be a better method of visualising the microstructure.

Light microscopy was used with an iodine stain in a 60% sucrose solution to look at the change in microstructure along a cross section of a sweet. Commercial sports mixture, as well as sports mixture recipe which was deposited in plastic moulds and not stoved, were studied. The microstructures were very different, highlighting the effect of processing on microstructure, with the commercial product having a bicontinuous structure with secondary phase separation occurring in the gelatine rich phase and the final solids product having a droplet morphology with gelatine as the discontinuous phase. The staining and cutting of the samples did not produce micrographs of high enough quality to

allow quantitative analysis and therefore a conclusion as to whether the concentration of gelatine is higher at the surface cannot be obtained. An alternative stain may prove to be more effective but overall light microscopy appears to give sufficient magnification to allow the phase behaviour of confectionery to be studied relatively quickly and easily.

Monitoring Conditioning

Clearly not enough research has been done to make firm conclusions and more needs to be done in this area. However, the limited results that are available lead to the following tentative conclusions: The elasticity of the wine gums increased during conditioning (as seen by a decrease in the relaxation value). This happens in wine gums that lost or gained moisture, or remained at a constant moisture content, suggesting that changes in the total moisture content are not important for conditioning. Changes in moisture content can only be detrimental; it risks moving acceptable wine gums outside the range of acceptable moisture contents and therefore conditions should be chosen to minimise this.

There were large variations in the initial texture, stickiness and masses of wine gums from different batches. The source of the variation in texture was not clear but it was evident that it was not entirely dependent on the moisture content. This was shown by two batches of wine gums having identical moisture content but substantially different textures. Therefore there is clearly another important factor that determines the texture other than the moisture content. The effect this initial difference has on the way wine gums condition is also not yet understood but there was some suggestion that samples which had a higher relaxation value changed texture at a slightly faster rate and took longer to reach equilibrium. If this is the case it would suggest that conditioning is not

only beneficial in terms of reducing the risk of deformation during packing but it also minimises the difference in texture between batches, giving more consistent products. This conclusion is very hypothetical and more experiments performed over longer time periods are necessary. The large variations in initial stickiness are particularly interesting because these appear to be larger than the changes caused by even the most extreme external conditions (i.e. 25°C/ 75%RH). This could mean that packing problems are being initiated at an earlier point in the manufacturing process and are not being caused by fluctuating conditions in the conditioning plant as is commonly thought. Further investigations are needed; these should initially concentrate on the impact that microstructure and quantity and coverage of oil have on stickiness.

In general, the external conditions were not seen to have a large impact on the texture and stickiness of the samples. The exception to this was the sample held at 25°C/75%RH but this was far outside the acceptable range for both temperature and relative humidity and caused the wine gums to absorb water to such an extent that they were no longer of acceptable quality. Changes in temperature seemed to have a greater effect on moisture movement than changes in relative humidity. Although the Bournville tests provided a hint that higher temperatures may be beneficial because the samples stored at 25°C reached equilibrium before the samples stored at 20°C (both 45%RH), the difference in texture over the entire duration was actually very small and probably within experimental error. In fact, considering all of the results obtained it seems that 25°C would actually be an unsuitable temperature for conditioning wine gums for several days due to the excessive movement of moisture. The factory temperature limit is 22°C. Although these results justify an upper temperature limit, more experiments would need to be performed before it could be said with certainty that 22°C is a suitable limit. Conversely, the factory relative humidity

limit is currently set at 55%RH and yet the results suggest that conditioning at 60%RH would not be in any way detrimental. The 75%RH tests showed that there should also be an upper relative humidity limit but again more tests should be performed in order to establish the exact value.

Although it has been proved that the change in total moisture did not cause the changes in texture seen during conditioning this does not mean that moisture movement within the wine gum was not the cause. The Karl Fischer results cannot be relied upon but support the hypothesis that there was a moisture gradient from the centre of the wine gums to the edge and that this gradient decreased during conditioning. However, there is not yet any evidence which shows that this diffusion of moisture caused the textural changes. Experiments were performed to identify whether the same changes occurred in samples that were uniform and constant in moisture content; the results suggested that these samples changed texture in a similar way to wine gums but more tests would need to be conducted before this could be conclusively stated.

Overall, the results began to aid the understanding of the conditioning process but far more experiments of this nature should be completed before any firm conclusions can be drawn.

Determination of Phase Diagram

Starch / gelatine phase diagrams at three different sugar concentrations were prepared. It had been anticipated that increasing the sugar would make the two polymers more miscible, reflected by a larger area beneath the binodal, up to a sugar concentration of 15%. Upon increasing the concentration further still it was expected that the excess sugar would promote demixing due to a competition for water, leading to phase diagrams with smaller one phase regions than those seen for solutions containing no sugar. However, this is not what

the results showed. Instead, all concentrations of sugar reduced the area of the miscible region on the phase diagram, i.e. sugar solutions at all concentrations were poor solvents compared with water. The work in this area needs to be continued. One of the main purposes of producing the phase diagrams was to find the critical concentration in order to understand where the commercial sports mixture recipe is in relation to this point. However, this was not achieved.

Chapter 7

Further Work

Quantifying and monitoring the changes which occur during conditioning is fundamental and so more work should be done on this area. The experiments could be repeated with sports mixture to ensure the results are comparable and each temperature and humidity environment could be checked using several different batches of sports mixture to ensure the results are reproducible and not batch dependent. A wider range of conditions should be used and the parameters should be monitored over at least a 3 day period.

Information which characterises consumer ready sports mixture should continue to be collected. If any changes are made to the manufacturing process in the future this data could then be used as a check to ensure the final product has not changed in any way. This is particularly important for the texture which would be readily identified by consumers.

The work on identifying whether it is moisture movement or gelatine network development which primarily causes the textural changes associated with conditioning should be finished. The conclusions drawn from this work will then dictate the most appropriate area to investigate. If this is found to be moisture,

related modelling using Comsol is likely to be important.

The phase separation results appeared interesting and not in line with expectations based on other biopolymer mixtures. Therefore, this could be investigated further to check whether the results are reproducible and if so, to understand the significance of these results.

Although the relative humidity of the conditioning areas have been shown to affect the stickiness of sweets, the data obtained in this thesis has particularly highlighted the large variation in stickiness between batches. Understanding the reason for this variation should be investigated further. It has been suggested that the oiling of the sweets during finishing is not well regulated and the residence time of the sweets in the oiling drum has gradually decreased. As a result the sweets are not being completely coated with oil. Experience at the Crediton factory suggests that both over and under oiling their products can lead to excess sticking of the sweets and problems packing. Therefore, the relationship between oiling and stickiness could be investigated. It has also been suggested that the microstructure could affect the stickiness and so the light microscopy work could be developed further to identify if there is a link between stickiness and the concentration of gelatine at the surface.

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