9 Food Structures Designed for Oral Response/Flavour Release

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9.1 INTRODUCTION

Flavour can have many definitions depending on the context. In this chapter, "flavour" refers specifically to the volatile aroma component of food. It is composed of a wide range of compounds, and may involve up to 10 000 different molecules, which are sensed by *ca*. 350 aroma receptors at the olfactory epithelium in the nose. It is distinctly different from taste, which generates the sensations of salt, sweet, sour, bitter and umami, which are sensed in the mouth. The complexity of the flavour component of foods is often the main character that distinguishes one food from another. Fruits, for example, can have similar attributes in terms of sweetness and acidity, but it is the flavour that differentiates the apple from the pear.

The different modes of sensing taste and aroma affect the impact of food structure on our perception of these components: tastants have simply to dissolve or pass into the saliva layers coating the tongue to reach the taste buds where they are sensed; flavour molecules, on the other hand, have to pass from the foodstuff into the in-mouth gas phase (typically passing through the saliva layer en route) before they can be transferred though to the throat where exhalation carries them up to the nose. Consequently, the passage of flavour from food to nose often involves many different transitions between phases, all influenced by the composition of the phases and the physical properties of the compounds themselves.

Although the taste and flavour components of foods have different paths by which they reach their receptors during eating, it is important for the consumer that the correct taste/flavour profile is sensed for any particular product. Often the taste/flavour profiles that are acceptable, or desired by the consumer are based on learning and repeated exposure

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during their lives (Blake, 2006). Modifications to food structure on the macro (restructuring of the whole food product) or micro (use of flavour encapsulants in flavour delivery) scale that alter flavour delivery must therefore deliver expected profiles, or new ones that the consumer is prepared to learn. The latter are often associated with changes in dietary patterns, such as the trend to lower salt, or low-fat-content foods, or the use of artificial sweeteners. In addition to the taste/flavour interaction, there will also be sensory inputs from vision, textural perception and trigeminal receptors, all influencing perception.

9.2 MEASURING FLAVOUR DELIVERY

With any stimulus it is important to know the intensity and timing of its delivery. Both factors will be key in converting the stimulus into perception. Both of these are essentially about detecting change in our environment, which is typically the main thing we notice. For example, we notice acceleration rather than steady-state velocity.

Until the 1990s it was not possible to observe the changes in volatile delivery to the breath during the eating process, these *in vivo* processes were effectively a black box. Both of the main methods of detecting flavour compounds in the breath are essentially similar, involving the use of mass spectrometers to ionise and monitor flavour molecules in real time (Taylor and Linforth, 2010). These techniques can detect flavour molecules at concentrations at or around their odour thresholds. However, in many studies with real foods, the levels of many flavour compounds are present in the breath at subthreshold levels, only generating an overall perceived stimulus through their combination with other flavour components.

The use of model systems, marker compounds and mathematical modelling (Linforth, 2010) have all combined to develop our understanding of the process of flavour delivery. Such knowledge is essential if we are to design and develop structures to deliver flavour to the consumer.

9.3 FLAVOUR PHYSICAL CHEMISTRY

The many flavour molecules that we sense when we eat food have a wide range of physical properties. They will vary in their water and fat solubility, which is characterised by the log *P* (log of the octanol–water partition coefficient) of the molecule. They will exhibit differences in their intrinsic volatility, which can be described by their vapour pressure. These factors affect the way in which molecules partition between

the different phases of foodstuffs and ultimately the efficiency with which they transfer from the food to the breath so they can pass to the nose. It is important to understand the impact of the physical chemistry of the flavour molecules when designing or modifying structures for flavour delivery.

Even the simplest of structures, water, does not release all compounds equally upon consumption. If all compounds were to deliver equally from solution in water (which also parallels their transfer from saliva when eating more complex foods) then they should all reach a level equal to a certain proportion of the maximum expected. In this case, the maximum we would expect any molecule to reach is that of the air–water partition coefficient at equilibrium. Flavour compounds have different air–water partition coefficients (the ratio of the number of molecules in each phase) depending essentially on their volatility and water solubility. If they all manage to achieve the same proportion of this thermodynamic equilibrium during consumption, they can be considered to deliver equally *in vivo*.

In the upper airway and mouth there are effectively small volumes of space with high gas flows passing through them (Linforth and Taylor, 2006). Consequently, volatile transmission from liquid phase to gas phase is restricted and for many compounds they do not achieve the concentrations expected on the basis of their air–water partition coefficient. Added to this is one further factor: the surfaces of the solutions *in vivo* do not mix with the bulk of the bolus, even if it is as mobile as water. This can result in the surface depletion of volatiles from the solution interface (with the breath) as it attempts to reach equilibrium (Marin *et al*., 2000). This depletion varies with the air–water partition coefficient because it is this that determines the proportion of molecules that have to transfer from the liquid to the gas phase to achieve equilibrium (Linforth *et al*., 2002).

Compounds with a low partition coefficient (e.g. pyrazine) have to transfer relatively few molecules from the liquid to the breath to achieve equilibrium and can achieve up to 60% of their equilibrium levels on consumption (see Fig. 9.1). Compounds with high partition coefficients need to transfer a greater proportion of molecules from the liquid to the gas phase to achieve equilibrium and deplete at the surface before this can happen. Consequently, compounds like α-pinene achieve a breath concentration far less than 1% of that expected on the basis of their air–water partition coefficients.

So important is the effect of the surface as the point of flavour delivery that compounds such as ethanol show enhanced delivery due to their ability to form a monolayer at the interface; thereby providing extra molecules for transfer to the gas phase. The ethanol monolayer can also enhance the delivery of other compounds (Clark *et al*., 2011),

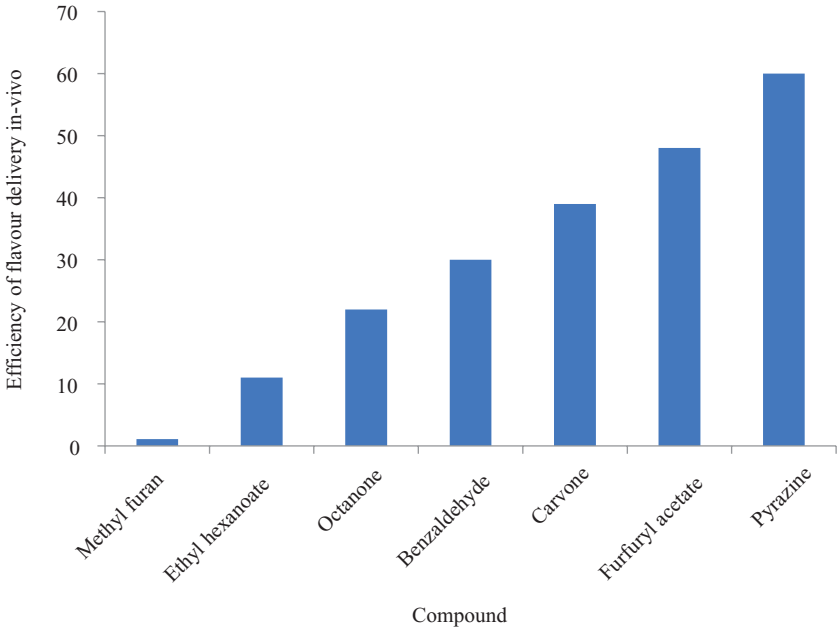

Fig. 9.1 Efficiency of *in vivo* delivery for compounds with different air–water partition coefficients. The partition coefficient decreases from left to right.

presumably through their co-solubilisation in the monolayer. Equally, carbonation of the solution results in the formation of increased surface area and mixing within the liquid, this again enhances flavour delivery (Clark *et al*., 2011).

9.4 FLAVOUR DELIVERY FOR COMPLEX SYSTEMS

With more complex flavour systems there is the potential for delivery directly from the bolus where the bolus–air partition coefficient will be the main factor affecting flavour delivery. This route may be very important for very hydrophobic compounds, which are limited in their capacity to enter the saliva phase (Taylor *et al*., 2001).

Structures delivering flavour via the saliva phase *in vivo* will have to dissolve into the saliva, as in the case of gels or boiled candies. Alternatively, the flavour can partition from structures that are more resistant to breakdown, such as chewing gum (de Roos, 2000).

When dissolution and breakdown of the bolus is the main route for flavour to enter the saliva, all flavour molecules are liberated at the same rate, whereas the saliva–bolus partition coefficient is the key factor affecting flavour transfer to saliva in more resistant structures.

Once the flavour has entered the saliva phase, it must migrate to the surface where saliva–breath partitioning will take place with efficiencies similar to those for the consumption of flavour molecules in water.

The migration of the flavour molecules to the surface can be through one of two main routes depending on the degree of mixing of food and saliva that occurs in-mouth (de Roos, 2000). The stagnant film route considers the in-mouth situation as static layers of saliva that do not mix significantly. Here the main factor affecting delivery of flavour from bolus to breath is molecular diffusion, a process that is broadly similar for all flavour molecules as small dissolved compounds (Marin *et al*., 2000). Diffusion can be a slow process limiting the transfer of flavour molecules to the interface (Marin *et al*., 2000) and may have a limited effect *in vivo*. The layers of saliva around the bolus are, however, limited in their thickness, because the main role of saliva is to provide a lubricating coat for the bolus to aid its transfer to the digestive tract.

The penetration route envisages eddy diffusion to carry a volume of flavor-laden saliva from the vicinity of the bolus to the saliva–breath interface. During the contact time of the flavour-laden saliva with the breath, flavour molecules can partition into the air, driven by the concentration gradient between the two phases. The volume of saliva containing the flavour may remain at the interface, or, through further mixing, may be moved back into the lower layers of saliva as new elements are carried to the interface.

Overall, structures designed to deliver flavour molecules to the breath during consumption are constrained by the physical chemistry of the compounds themselves (polarity, volatility and phase partitioning behaviour). Equally, they are dependent on the physical processes taking place in-mouth and any changes in oral processing that they cause.

9.5 FLAVOUR RELEASE FROM HOMOGENOUS SYSTEMS

In homogenous systems the flavour is uniformly distributed throughout the bolus at the same concentration. Equally, the structural properties of the bolus are similar throughout, such that oral processing and release can take place in a similar way from any part of it. These systems vary in their mechanical properties from thickened solutions through to gels and hard-boiled candies.

9.5.1 Flavour delivery from thickened solutions

Early work, (Pangborn and Szczesniak, 1974) showed that increasing concentrations of hydrocolloid thickeners would decrease the percep-

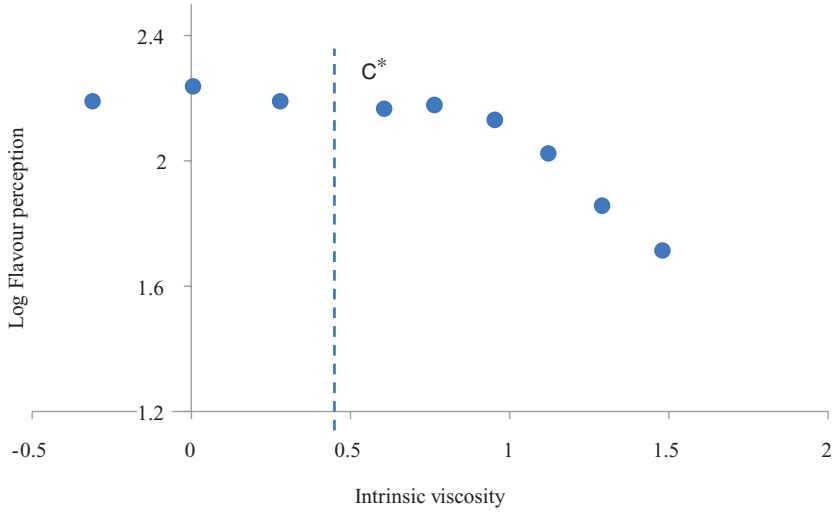

Fig. 9.2 Effect of increasing guar concentration on flavour perception.

tion of the flavour when aqueous solutions of flavour compounds were consumed. Further work by Baines and Morris (1987) showed that this phenomenon started at *C**. Below *C** there was little effect of the hydrocolloid thickeners on the perception of the flavour compounds, whereas above *C** there was a progressive decrease in flavour perception as the concentration of the hydrocolloids increased (see Fig. 9.2).

*C** is the point at which the concentration of hydrocolloids in a solution increases beyond the stage at which the hydrocolloids are separate from one another in solution. At this point these macromolecules become entangled with one another and start to form a three-dimensional network resulting in an increase in viscosity of the solution.

This increase in viscosity was thought to decrease the diffusion of flavour compounds to the interface, minimising delivery of aroma compounds to the olfactory epithelium *in vivo*. Several studies were performed analysing the concentration of aroma compounds in the headspace above thickened systems in order to try and understand the mass transfer of flavour under these conditions (reviewed in Lubbers, 2006). However, headspace analysis may differ from *in vivo* delivery due to differences in gas flows and the movement of the sample/bolus (Linforth and Taylor, 2006).

For some of the headspace systems studied there appeared to be a chemical binding interaction between the hydrocolloid thickener and the flavour molecules themselves. This is consequently less an influence of structure and more one of chemistry and is of less relevance to

this discussion. Other studies showed an influence of thickeners, decreasing the headspace concentration of aroma compounds. This did, however, vary with the air–water partition coefficient of the compounds, with compounds with lower partition coefficients showing less impact of the hydrocolloids on their headspace concentration.

As discussed earlier, this phenomenon can be explained by the effect of the air–water partition coefficient on surface depletion of flavour compounds as the system tries to reach or maintain its equilibrium state (Marin *et al.*, 2000). Beyond this, the differences in the headspace concentration may largely be explained by the effect of the hydrocolloids decreasing the mobility of the bulk system. This will decrease the potential for delivery of sample and consequently flavour from the aqueous phase to the interface. This will further increase the effect of the air–water partition coefficient on flavour depletion at the sample/air interface. However, it is worth remembering that headspace analysis may differ from *in vivo* flavour delivery.

Actual measurements of *in vivo* flavour delivery (see Fig. 9.3) showed that there was little impact of hydrocolloid thickeners on flavour delivery as samples increased in viscosity (Cook *et al.*, 2002; Hollowood *et al.*, 2002). The hydrocolloid thickeners were not decreasing processes such as diffusion or the penetration route of flavour delivery. In terms of flavour delivery they must have been forming the same effective surface area for flavour delivery during the consumption process.

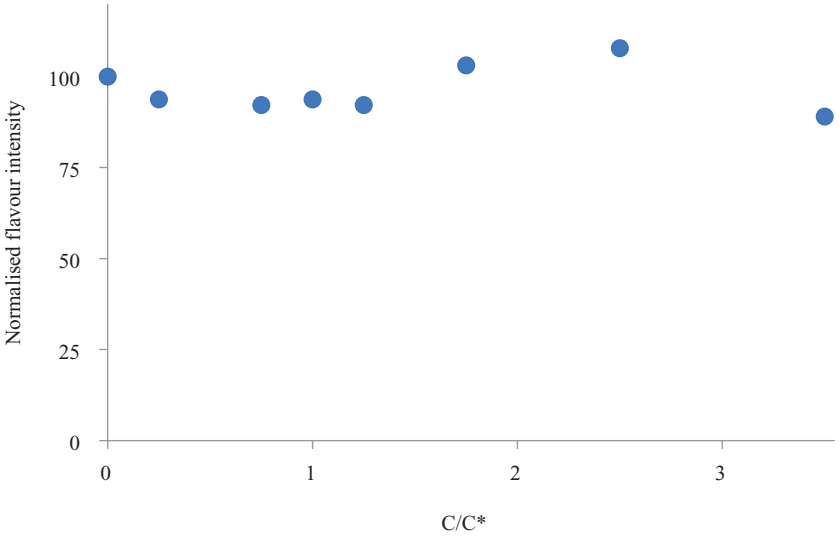

Fig. 9.3 Intensity of isoamyl acetate *in vivo* flavour delivery (average for three thickeners) as a function of concentration *C* relative to *C**.

If flavour delivery was similar between thickened and unthickened solutions, what could be causing the differences in perception? One possibility is that the perception of the thickened state of the sample has an effect at the cognitive level. This reduces the integration of the flavour stimulus that has been delivered, in the formation of a recognised perceptual event. Equally, it has also been observed (Baines and Morris, 1987; Cook *et al*., 2002; Hollowood *et al*., 2002) that increasing the thickness of samples used in these experiments decreases the perception of the taste component of the samples (the samples typically contained sugar to make them more palatable to the panellists). The decrease in taste perception will impact on the cognitive integration of the combined taste/flavour stimulus, which may account for the overall decrease in flavour perception (Salles, 2006).

Further work by Cook *et al*. (2003) found that the viscosity of solutions measured under conditions that mimicked the in-mouth oral shear characteristics (Elejalde and Kokini, 1992) could be used to model changes in perception of thickened solutions during consumption. This applied not only to hydrocolloids that exhibited entanglement and overlap at C^*, but also to thickeners with no distinct C^* point, or those that were also shear thinning.

Overall, it appears that adding hydrocolloids to thicken solutions has little impact on flavour delivery to the olfactory epithelium during *in vivo* consumption. The change in the structure of the food matrix from water to more structured systems does, however, affect perception through other mechanisms.

Aprea and co-workers (2006) studied the effect of hydrocolloid thickeners in custards, to investigate how differences in viscosity affect flavour delivery. The flavouring comprised of three esters with 0.1 or 1.0% carboxymethyl cellulose (CMC) added to the custard. When using a natural eating style, the panel showed no overall significant differences in the maximum intensity of flavour delivery, time to maximum, or the overall area under the release curve.

The results for the panel were further broken down into panellists who consumed the samples quickly (ST group), and those who took longer to consume them (LT group). Overall the LT group released more flavour from the 0.1% CMC samples, whereas the ST group released more flavour from the 1.0% CMC samples. The differences were interpreted as dependent on the rates of mass transfer for the two products, with the LT group increasing delivery from the 0.1% CMC samples, because these samples had a higher mass transfer potential. For the ST group the thicker sample was associated with a longer swallow time, resulting in more time for flavour delivery.

It is likely that changes in sample texture can modify the eating pattern of groups of people differently. The impact of texture on our

eating styles and flavour delivery is poorly understood, although many studies have been conducted on dental state, eating habits and appetite. Whatever the cause, it is clear that modifications to sample structure may not result in uniform changes in flavour delivery within a population, dependent on our eating styles. This may in turn affect our preferences for one food relative to another.

9.5.2 Effect of gels on flavour delivery

Further structuring of the food system can take place as the hydrocolloid concentration is increased. This results in the formation of gels, which are effectively semi-solid to solid systems. These have also been reported to decrease the perception of flavour as a function of increasing gel strength (Guinard and Marty, 1995).

The changes in perception were (as in the case of thickened solutions) attributed to major changes in the intensity of flavour delivery. However, a series of studies of flavour release from gels showed only minor changes in flavour delivery. Weel and co-workers (2002) studied the release of diacetyl and ethyl butyrate from a range of protein-based gels. There was a 15-fold difference in the hardness of the weaker gels compared with the strongest. These resulted in significant differences in sensory perception for both compounds, with the weaker gels producing the strongest perceived flavour release. *In vivo* studies of actual flavour delivery showed no differences in delivery in either the intensity or the temporal dimension.

The similarities in flavour release between the gels may have been due to their protein-based structure: this will have fractured to create the surfaces for flavour delivery. Clearly from their findings, the breakdown of the gels on eating was sufficient for all gels to achieve the same rate of delivery. The differences in perception may therefore be a direct result of textural perception of the gel hardness. Consequently, when structures are manipulated in order to modify flavour delivery, any secondary effects influencing texture may also impact on the perception of the flavouring.

Baek and co-workers (1999) used a series of gelatine gels flavoured with furfuryl acetate. These will have both broken down and melted during consumption, changing the flavour release pattern. Sensory analysis showed that increasing the gelatine concentration from 2 to 8% decreased the intensity of perception and also delayed the timing of release (see Fig. 9.4). The 8% gel was perceived with a flavour intensity of only 30% of that of the 2% gel.

Instrumental analysis showed the same trend in the temporal dimension with the T_{max} increasing with gelatine concentration (see Fig. 9.5). The changes in the intensity of flavour delivery were, however, much

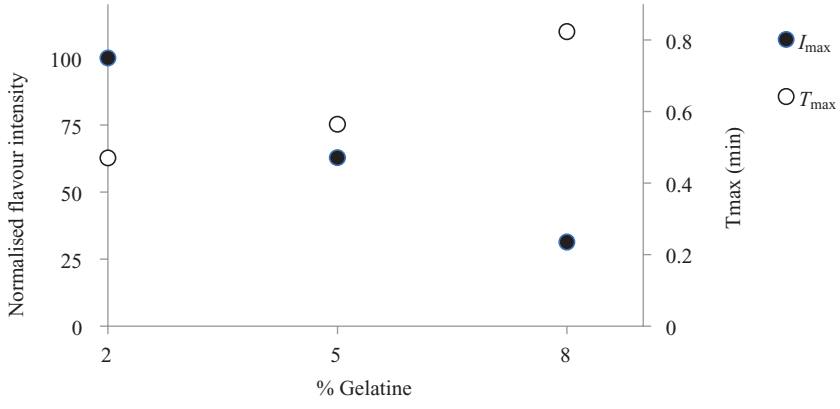

Fig. 9.4 Sensory analysis of 2, 5 and 8% gelatine gels for the intensity (I_{max}) and timing (T_{max}) of flavour release.

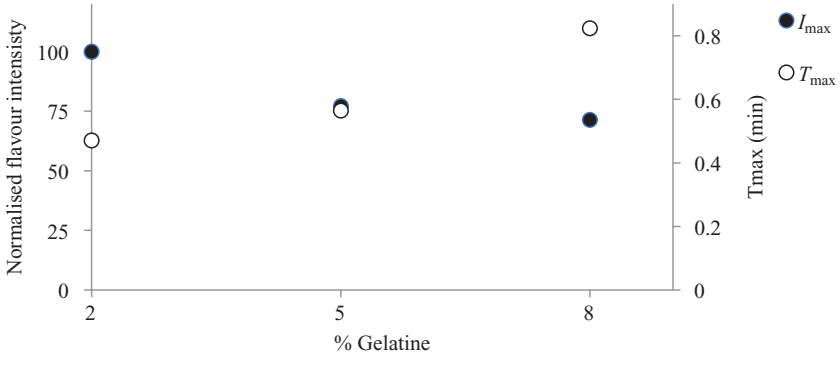

Fig. 9.5 Instrumental *in vivo* analysis of 2, 5 and 8% gelatine gels for the intensity (I_{max}) and timing (T_{max}) of flavour release.

smaller than expected based on the sensory data. The 8% gel I_{max} was 70% of that of the 2% gel.

Humans have a limited capacity to discriminate between samples of different flavour intensities, typically requiring a 25–40% difference in flavour delivery to notice a difference. The strong perceptual differences between the samples was attributed to the differences in the timing of delivery with the longer slower release profile being perceived the weakest. There is, however, the potential for other attributes, such as the increase in gel hardness, or, the changed release profile for the taste compounds (all gels contained sugars) to have affected the perceived flavour intensity. Structures designed to modify the intensity of flavour delivery need to take into account any secondary effects on the timing of flavour release and any impacts on taste delivery.

9.6 FLAVOUR DELIVERY FROM HETEROGENEOUS SYSTEMS

9.6.1 Layered flavour

One of the simplest means of phase separating flavours is not to distribute them uniformly throughout the food matrix, but to incorporate them into specific regions or layers of the food matrix. Pearson (2005) investigated the effect of this on *in vivo* flavour release using both sensory and instrumental analyses. In the first set of experiments, a range of compounds with different physico-chemical properties (limonene, hexanol, linalool and methyl acetate) were incorporated into gelatine–sucrose gels in one or more layers, such that the total amount of flavouring was the same in each sample of gel (see Fig. 9.6).

The analyses showed that flavour delivery was similar from each of the gels in both the intensity and timing of flavour delivery. This was attributed to the changes that happen to the gels during consumption. The gels fractured on chewing and were quickly broken down into many small fragments that subsequently dissolved into the saliva. The many fragments mixing with saliva would have resulted in a similar saliva flavour content, which would then partition with the in-mouth breath, negating any influence of the initial flavour distribution.

The effect of layering was further investigated in a series of layered chewing gum samples with the flavour (ethyl butyrate and ethyl acetate) added throughout the sample, in up to 16 layers. Here the release mechanism may be different from that of the gels since the chewing gum does not fragment and dissolve during consumption. This system also showed no significant effect of dispersion of the flavouring in layers, when compared to the homogenously flavoured product. This was thought to be due to the mixing of the layers by the action of chewing quickly minimising any potential for differences in flavour delivery. This is consistent with the findings of Prinz (1999), who observed that 20–30 chews were enough to totally mix the layers of a chewing gum sample during eating.

Fig. 9.6 Flavour incorporation into layered gels. Each gel was 20 mm deep and layers were either flavoured (black) or unflavoured (white).

9.6.2 Encapsulated flavours

In addition to systems where the flavour is phase separated through its distribution in different parts of the food matrix as dissolved flavour, the flavour compounds may also be present in a form where it is entirely separated from the matrix. This typically takes the form of encapsulated flavour where the flavour is isolated in individual structures, from which it is subsequently released during consumption.

Encapsulation systems offer several advantages for flavour delivery. They can minimise the exposure of the flavour to air, or to components of the food matrix which would degrade them. For example, aldehydes react with amine groups to form a Schiff base resulting in their loss, decreasing their potential for flavour release. This may result in the loss of vanillin in biscuit manufacture, as vanillin reacts with proteins or other amino groups in the food matrix. Encapsulated flavours can also be easier to handle within the food manufacturing process and facilitate dispersion of the flavour throughout the product.

However, in order to function, the encapsulated flavour must release the flavouring to the consumer at the point of consumption. If the flavour is too protected and fails to release to the consumer, then it would in itself, effectively result in flavour loss.

9.6.3 Flavour release from droplets

Linforth *et al.* (2007) created a series of gel samples with either dispersed flavour, or, highly concentrated flavour in one or more droplets (see Fig. 9.7). This was achieved by physically injecting flavour compounds into gel samples with a syringe as they were setting. This represents one of the most extreme separations of flavour from the product matrix, to determine how this affects flavour delivery.

During consumption of the flavour droplet systems, there was a substantial increase in *in vivo* flavour delivery, relative to the samples with similar flavour contents, but which had the flavour dispersed throughout the gel. The authors suggested that the presence of flavour

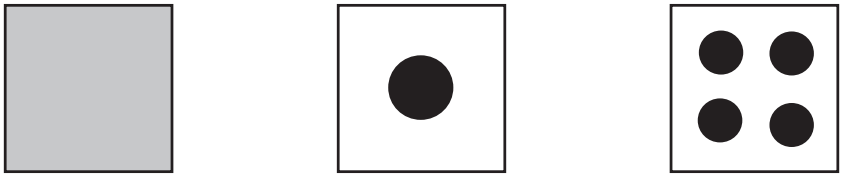

Fig. 9.7 Cubes of gels containing either; left, dispersed flavour; centre, one droplet of flavour; or, right, several droplets of flavour.

in droplet form (rather than dispersed) resulted in a different mechanism of flavour delivery. They suggested that the droplets of flavour were released from the gel through mastication and passed to the air–saliva interface with minimal dissolution or dispersion in the saliva. Once at the air–saliva interface, surface tension caused the droplets to spread out on the saliva surface. This resulted in a thin layer of flavour directly exposed to the breath, into which it could volatilise. Typically, this resulted in intense flavour delivery early in the eating time course, and this continued throughout the eating process. In contrast, the dispersed flavour samples had a slower onset of flavour delivery and a later maxima, as the delivery of flavour required the fragmentation and dissolution of the gel before flavour could enter the saliva phase and partition into the breath.

Such a delivery mechanism bypasses the dissolution of flavour compounds from the foodstuff into saliva and the subsequent partitioning of flavour compounds into the breath. Flavour delivery is now more dependent on the intrinsic volatility of the substance than its air–saliva partition coefficient.

However, the increase in flavour delivery was not the same for all compounds and depended on their physical properties. This was characterised by the log *P* and the vapour pressure of the compounds. Compounds were more likely to transfer from the saliva surface if they were more volatile, with higher vapour pressures. However, compounds with very high vapour pressures also tended to be small compounds with low log *P* values and reasonably water soluble. These tended to disperse and dissolve in the saliva, reducing their potential to deliver directly from the air–saliva interface. Consequently, the compounds which showed the greatest difference in release were those of intermediate polarity and volatility. These were sufficiently volatile to transfer into the gas phase and hydrophobic enough to minimise dispersion and solubilisation in saliva. The differences in delivery between the dispersed and droplet forms of the gels could be substantial for these compounds. Ethyl hexanoate showed the largest differences, with 2400-fold more delivery from the droplet-containing gel than when the flavour was dispersed.

The presence of flavour as a single droplet within a food product is clearly an extreme example of food–flavour separation. The effect of distributing the flavour as smaller and smaller droplets was investigated (see Fig. 9.7). This showed a decrease in the maximum intensity of flavour release with increasing droplet number (Pearson *et al.*, 2007). The effect may, however, remain with food systems which contain a number of small droplets of flavour within the food matrix. This would include systems such as pressed mint sweets, where the flavour is trapped, rather than dissolved with the matrix, and many encapsulation

systems where the flavour is phase separated. These systems may enhance flavour delivery, depending on the physical properties of the flavouring.

9.6.4 Encapsulating flavours within pre-formed structures

One of the options when encapsulating flavours is to form the structure of the encapsulant around the flavour during the encapsulation process. Another option is to take a pre-formed structure and enhance its flavour delivery potential. Yu *et al*. (2012) used coffee granules and incorporated nitrogen into the structure to act a vehicle for increased flavour release.

To get the nitrogen to enter the coffee granules, the granules and the nitrogen (40 bar) were heated together in a sealed vessel. The increase in temperature affected the physical state of the coffee granules, because it was increased beyond the glass transition temperature. Under these temperature and pressure conditions the nitrogen passed into the granules. The system was subsequently cooled and depressurised, leaving the nitrogen trapped within the structure.

The modified coffee granule structure could later be induced to release the entrapped nitrogen and flavour when added to water, resulting in the dissolution and dispersion of the granule structure itself. This gave a pulse of flavour release relative to coffee granules that had not had the nitrogen introduced into their structure (see Fig. 9.8).

In this case there was an increase in flavour delivery from the flavour within the coffee granule. It would be interesting to further develop such systems, choosing an unflavoured pre-existing structure and pressurising it in the presence of added flavour, potentially adding both

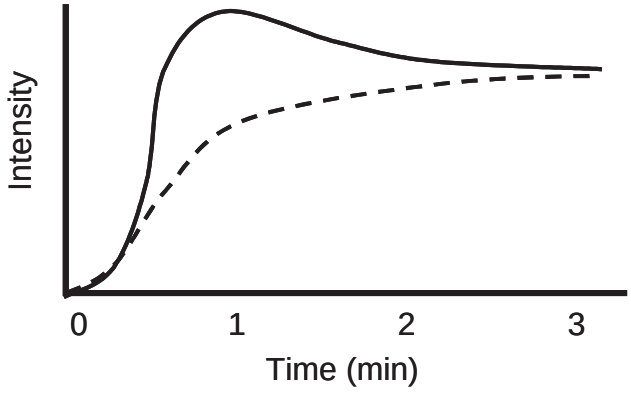

Fig. 9.8 Differences in delivery of coffee aroma from coffee granules added to water (dashed line) and coffee granules pressurised with nitrogen (solid line).

nitrogen and flavour to the structure. This would allow a pre-formed encapsulation system to be flavoured with a range of flavours on demand, requiring only the storage of the system and neat flavours, rather than the bulkier alternative of preparing and storing a range of flavours in an encapsulation matrix.

9.6.5 Polymeric entrapment of flavours

A range of matrices can be used for the encapsulation of flavours that rely on the immobilisation of the compounds in a solid matrix. These can be based on polymers such as starch, gum arabic or proteins, often in combination with other smaller components which act as modifiers to the encapsulant structure (Madene *et al*., 2006). Modification of the structure impacts on the density and permeability of the structures formed, which ultimately affects their behaviour during flavour release and delivery during consumption. There are a range of methods for producing flavour encapsulation systems, from co-extrusion of the flavouring material to spray drying. Many of these processes involve heat to form the final product. However, due to limited time exposure even thermally labile compounds are largely unaffected.

During spray drying, a polymer solution and a carrier containing the flavouring are nebulised in a stream of hot air, which dries the system (see Fig. 9.9). The polymeric material forms a coating around the flavouring, resulting in a stable encapsulant powder. Depending on the operating conditions, this can be an effective, inexpensive, continuous process for encapsulant production. However, very volatile components of a flavour system may be lost and the material that should form the protected core of the system may also end up on the surface, where it will be exposed to chemical degradation.

In extrusion the flavour is dispersed in a polymer matrix and this is extruded through a die. It then enters a drying liquid that hardens the extrudate and traps the flavour in the polymer matrix. This can result in polymer systems with defined properties of stability and release depending on the construction of the matrix (Benczédi, 2010). The permeability and diffusion in such system that protects the flavour and controls its release is, however, dependent on cracks, pores or other defects in the surface of the extrudate. In addition, flavourings can vary widely in their hydrophobicity, from non-polar limonene through to polar molecules such as diacetyl. This in turn affects their behaviour and interactions within the glassy state.

Release from the glassy state is dependent upon the degree of crystallinity in the structure (Benczédi, 2010). Crystalline structures, by their very nature, exclude other molecules and will resist diffusion or release of molecules through them. Greater release and diffusion can

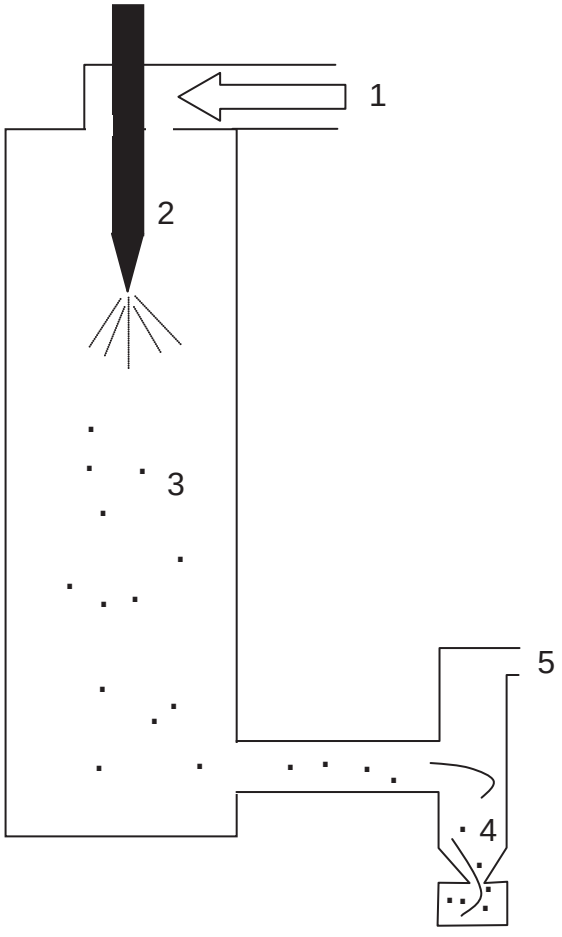

Fig. 9.9 Schematic of spray drier where a hot air stream (1) passes around the nebulised flavour-carrier polymer system which enters as a liquid (2) and enters the drying chamber (3) before passing to the cyclone (4) where the spray-dried material is separated from the drying gas that exits via an exhaust (5).

occur in amorphous regions of the encapsulant. However, rapid hydration during consumption will generate release at far greater rates than diffusion as the matrix disperses. Diffusion is effectively a more long-term consideration during storage, where humidity may be an issue. Harvey and Barra (2003) measured the *in vivo* release of peppermint oil from extruded encapsulation systems in chewing gum. These showed a clear burst of extra flavour delivery into the breath during the first few minutes of consumption. Here it is likely that the encapsulant protected the flavour from dissolution in the gum base, allowing a more efficient release of the flavour direct from the encapsulant into the saliva.

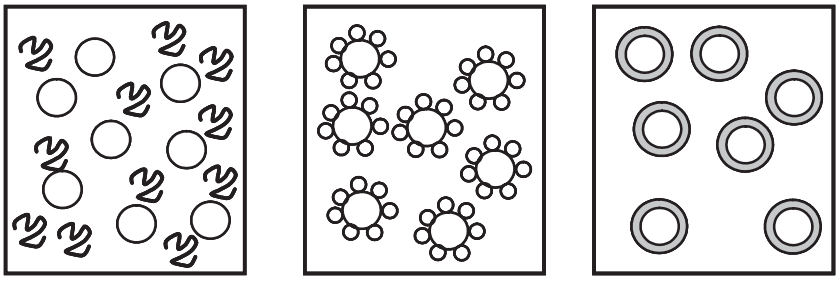

Fig. 9.10 A flavour dispersed in a solvent containing a biopolymer undergoes a change in pH causing surface association of the polymer at the interface of the two phases. Further changes in pH, temperature and the introduction of chemical agents result in crosslinking, forming the bonded coat of the coacervate.

In coacervation the material to be encapsulated (the flavouring) must not dissolve in the bulk fluid used to dissolve the polymer(s) that ultimately coat and encapsulate the product (see Fig. 9.10). Under constant stirring, the polymers absorb to the surface of the flavouring within the solvent system forming a layer on the surface. The coating by the polymer can be induced in a number ways, such as the addition of solvents, salts, or thermal- or pH-induced changes. Once the droplets are surface coated, the surface coating can be chemically or thermally crosslinked to fully encapsulate the core material.

Coacervates using gelatine of different bloom strengths as the coacervation polymer showed differences in the intensity of ethyl hexanoate release (Malone and Appelqvist, 2003). The 100 bloom coacervates showed much more intense flavour delivery than the 250 and 300 bloom strength gelatine coacervates, which were similar in their in-mouth release profiles. These differences were attributed to the melting point of the gel structure of the coacervates. The 100 bloom strength coacervates would have melted at around 23 °C resulting in substantial melting and release of flavour in-mouth, whereas the 250 and higher bloom strength gels would have melted at temperatures much closer to the in-mouth temperature, which restricted flavour delivery. In addition to bloom strength, the coacervates could be manipulated by crosslinking the gel structure. This resulted in much slower rates of melting which would, in turn, decrease or delay the delivery of flavour (Malone and Appelqvist, 2003).

Multilayer systems can also be developed for the encapsulation of flavours. These systems allow regulation of the charge, thickness, porosity and permeability of the encapsulant. These are constructed using the physical properties of the components themselves to form the layers of the system. The key properties are those dependent on charge,

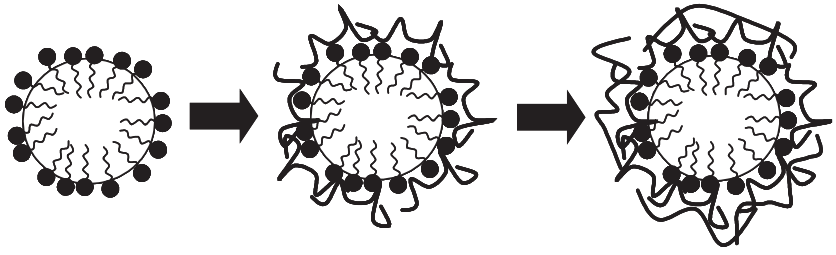

Fig. 9.11 Development of a multilayered system from a simple emulsification of the carrier matrix, through to the addition of one or more biopolymer layers.

such as electrostatic forces, or polarity-driven hydrophobic interactions. A hydrophobic system such as lipid can be emulsified with surfactants and then this can be coated with additional layers in sequence (McClements, 2009). A biopolymer with opposite charge can be bound to that surface as a further layer and the process repeated sequentially to produce more and more complex structures (see Fig. 9.11)

The charge and solubility of surfactants will affect their interaction with layers of biopolymers, which can include proteins or polysaccharides. The interactions between surfactants and biopolymers, and biopolymer–biopolymer interactions will again depend on pH and other solutes such as salts, both of which affect the ionic nature of solvents and solutions. Multilayered systems are dependent upon a range of components, each of which will have their own contribution towards the stability of the system. As such, multilayered systems can provide greater protection than simple systems, which are dependent on the properties of one or two components alone (McClements, 2009)

Depending on the exact nature of the system (crosslinking of the matrix etc.), flavour release will either be through solubilisation of the flavouring as it is released from the encapsulant system, or through the release of the flavour as small droplets. These will then either behave as dissolved flavor, and partition into the gas phase, or migrate to the surface for volatilisation directly into the gas phase, potentially enhancing flavour delivery.

9.6.6 Tailoring encapsulants for *in vivo* release

Malone and Appelqvist (2003) designed a series of encapsulants, which used lipid as a flavour carrier for lipophilic compounds. The lipid phase was encapsulated in structures that would release the flavour (ethyl hexanoate) with different trigger mechanisms, which included hydrolysis by enzymes, mechanical fracture and melting (see Fig. 9.12).

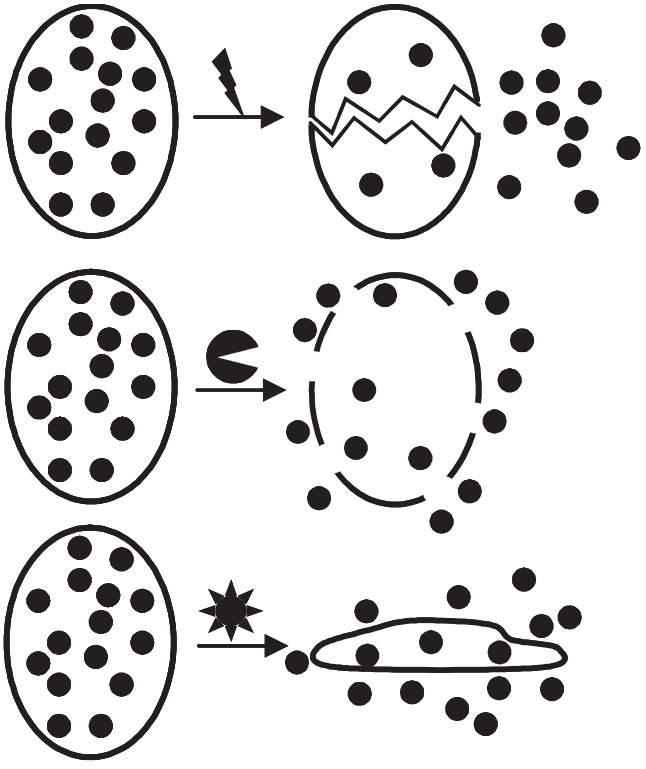

Fig. 9.12 Mechanical fracture, enzymic hydrolysis and melting of gels inducing flavour release.

Enzymic release relied on the action of α-amylase to hydrolyse starch, thereby releasing the flavour. These were prepared by gelling the flavour emulsion in starch at 95 °C. Release differences between starch types were observed based on the amount of amylose present in the gel particles. The wheat starch contained around 20% amylose, which resulted in firmer gel particles, which, in turn, resulted in a lower level of release when attacked by α-amylase. The other starch encapsulant was based on amaranth, which had a lower amylose content. This formed softer gel particles, which were observed to not only degrade due to the actions of α-amylase, but also to fracture when eaten, resulting in greater release of the flavour.

The second series of encapsulants were based on gel structures that relied solely on mechanical fracture during consumption to release the flavour. Here the mechanical strength of the gel particle could be altered to vary the release properties of the encapsulant. If the gels were prepared with 3% agar, they were firm and did not tend to fragment in the mouth. This resulted in an early peak of flavour release that decreased

over the following 2 minutes. In contrast, the 0.5% gels showed the same initial flavour release followed by continuous sustained delivery at this level over the 2 minute time course. The greater release from the 0.5% gels compared with the 3% gels was attributed to the extent of mechanical failure in-mouth. The 0.5% gels were much weaker than the 3% gels and tended to fracture far more readily, resulting in the different release profile.

Alternative gel structures relied on gelatine as the gelling agent to encapsulate the flavoured emulsion. By varying the gelatine concentration, the rate of in-mouth melting could be manipulated. The 2% gelatine gels initially retained the flavour and then released it, reaching a maximum at around 60 s. The 5% and 10% gelatine gels melted at much slower rates, showing later release maxima at 75 and 90 seconds respectively. All three gels had similar release maxima, demonstrating that this approach was affecting the timing rather than the intensity of release.

Overall, the tailored encapsulant systems represent approaches to flavour delivery where the mechanism of release is highly dependent upon the physical properties of the encapsulant, and its interaction with the human eating pattern. This can exploit different features of our physiology and oral processing to control the intensity and timing of flavour delivery.

9.7 SUMMARY

The delivery of flavour during eating is highly dependent upon the structure and physical properties of the food. The impact of these food structure differences will, however, vary as a result of the different properties of the flavour molecules themselves. Simple structural changes, such as the thickening of solutions or the formation of a gel, seem to have little direct effect on flavour delivery. However, these systems have a major impact on our perception of the flavour through other effects such as modifying taste perception. Such factors must be taken into account when manipulating food structure, either to modify flavour delivery, or simply to change the food stuff itself.

Complex structures can be formed to increase flavour delivery, alter the timing of flavour delivery, or simply to protect the flavour from reaction with the food stuff and the general environment. These vary widely in their attributes and are often tailored for specific foodstuffs, where the additional components will be acceptable. Overall, they are key tools for regulating the delivery of flavour and the creation of new generations of food products.

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