Factors Affecting the Release of Flavor Encapsulated in Carbohydrate Matrixes

Yvonne M. Gunning,[†] Paul A. Gunning,[†] E. Kate Kemsley,[†] Roger Parker,*[,†] Stephen G. Ring,[†] Reginald H. Wilson,[†] and Anthony Blake[‡]

Food Quality and Materials Science, Institute of Food Research, Norwich Research Park, Colney, Norwich NR4 7UA, United Kingdom, and Corporate R&D Division, Firmenich SA, 1 Route des Jeunes, CH-1211 Geneva 8, Switzerland

The effects of water content and tempeature variation on the release of flavor components into the headspace over flavors, encapsulated by an extrusion process, in low water content carbohydrate matrixes is studied. The largest amounts of release occurred when the matrix was above its glass transition temperature, whether this was due to increased water content or elevated temperature. Under these conditions up to 70% of the sucrose in the matrix crystallized over a period of 10 days, as quantified using Fourier transform Raman spectroscopy. Smaller amounts of headspace release occurred when the water content of the encapsulated flavor system was decreased from 3.5 to 3.1% w/w. Small amounts of release occurred from the "as prepared" materials, which were associated with the presence of small amounts of unencapsulated flavor oil with direct access to the headspace. It was concluded that release due to matrix permeability was relatively slow as compared with the above mechanisms.

Keywords: *Encapsulation; flavor release; differential scanning calorimetry; glass transition; headspace gas chromatography; Fourier transform Raman spectroscopy*

INTRODUCTION

Encapsulation of flavors and other food ingredients in solid matrixes allows them to be handled as free-flowing powders with limited evaporation of volatile components prior to their usage (Shahidi and Han, 1993; Blake, 1994). The rational design of encapsulation systems requires a physicochemical understanding of the mechanisms by which components are encapsulated and released (Whorton, 1995; Whorton and Reineccius, 1995; Goubet et al., 1998).

Much progress has been made in understanding the mechanism by which volatiles are retained during spray-drying (King, 1988; Rosenberg et al., 1990) and freeze-drying (Flink and Karel, 1970; Rifa and Voilley, 1991) and the subsequent storage of the resulting low water content products. The present study is concerned with volatile release during storage, which shares some common mechanisms with the retention of volatiles during drying processes. During storage the physical conditions are relatively limited compared with the wide range of temperatures and water contents that occur during processing by spray- and freeze-drying. However, qualitatively, similar processes occur, with partitioning between phases and diffusive mobility in the matrix being important considerations. Two basic mechanisms have been proposed to explain volatile retention during storage (Omatete and King, 1978; Voilley, 1995). Flink and Karel (1970) proposed that below a critical water content the volatiles become localized in "microregions" encapsulated within an impermeable matrix. Thijssen (1971) observed that, as water content is reduced, the diffusion coefficients of the volatiles decrease to a considerably greater extent than the diffusion coefficient of water, a process which was termed "selective diffusion".

It is important to recognize that studies of release mechanisms in biphasic systems require distinctly different approaches as compared with single-phase systems. For example, in the work of Karel and co-workers, methyl linoleate (Shimada et al., 1991; Labrousse et al., 1992) is essentially wholly immiscible with low water content lactose-based matrixes and is biphasic, that is, an emulsion, whereas small amounts of propanol (Levi and Karel, 1995) are likely to be wholly miscible with low water content amorphous carbohydrates and form a single-phase system. The work of Flink and co-workers provides a further example; in his earlier work Flink (Flink and Karel, 1970) considered the retention of volatiles including *n*-alcohols ranging from methanol to pentanol and, in later work (To and Flink, 1978), this was extended to include hexanol. Whereas the lower alcohols are fully miscible with the water, hexanol has an aqueous solubility of 0.6% w/w at 20 °C (Valvani et al., 1981). Little is known about the effect of carbohydrate on volatile solubility, but from the sucrose−acetone−water phase diagram (Bubnik and Kadlec, 1995) it is clear that the solubility is very much decreased, acetone becoming partially miscible with sucrose in concentrated solutions. Clearly the lactose−hexanol mixtures studied by To and Flink are biphasic with little mutual solubility. The structure of the biphasic system affects release; for example, if the droplet phase is completely immiscible, it will have to be at the surface to be released. If it is initially fully

* Author to whom correspondence should be addressed (telephone 44-1603-255396; fax 44-1603-507723; e-mail parker@bbsrc.ac.uk).
[†] Institute of Food Research.
[‡] Firmenich SA.

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enclosed by the matrix, it will have to break the surface to achieve release. By contrast, the components in a single-phase system can simply diffuse to the interface to achieve release. Flavors contain components that range from ionic and polar hydrophilic species to nonpolar hydrophobic species. If a flavor contains sufficient hydrophobic material, it forms an emulsion when mixed with water or other similar solvents. Flavor components partition between the hydrophobic droplet phase and the hydrophilic disperse phase, depending upon their relative affinities for the two phases. For those species that are present at significant levels in both phases, two-phase transport mechanisms need to be considered.

The glass transition of spray-dried (Whorton and Reineccius, 1995) and freeze-dried (Shimada et al., 1991; Labrousse et al., 1992; Levi and Karel, 1995) products has been related to volatile release, structural collapse, matrix crystallization, and extractable oil. Although the glass transition is clearly related to the material properties of the matrix (e.g., its viscosity) and rates of crystallization, there is growing evidence that in the glass transition region small molecules are more mobile than might be expected from the high viscosity of the matrix (Parker and Ring, 1995; Noel et al., 1995). There are relatively few measurements of diffusion coefficients in amorphous low water content carbohydrate systems (Menting et al., 1970; Arvanitoyannis et al., 1994; Parker and Ring, 1995) with which to quantitatively test "glass theory" predictions of small molecule mobility.

This study investigates the effects of variations of temperature and water content on the release of flavor components that have initially been encapsulated, by an extrusion process, in low water content carbohydrate matrixes. The aim is to understand the mechanisms of encapsulation and release by subjecting the encapsulation system to different conditions. One important distinction is between mechanisms whereby flavor can directly access the headspace and those which involve permeation through the matrix. Under certain conditions crystallization of the sucrose component of the matrix was observed, which was quantified using Fourier transform Raman spectroscopy. Measurements of glass transition temperatures of the carbohydrate matrixes allow the observations of crystallization and release to be related to glass transition behavior.

MATERIALS AND METHODS

Materials. Model cherry and peppermint flavors were encapsulated as emulsions dispersed in low water content (typically) amorphous carbohydrate matrixes. The materials were prepared using an extrusion process, as described by Risch (1988). The flavor oil is dispersed in a low water content carbohydrate (sucrose/maltodextrin) melt, which is then extruded through a die template, under pressure, into a chilled (~4 °C) 2-propanol bath. The bath is stirred by a stainless steel impeller, which breaks the product into short rods that are removed from the bath and dried. The flavor oil is fully contained during its dispersion in the carbohydrate melt with minimal headspace, and so there is little opportunity for preferential losses of flavor components. This means that it can be assumed that the composition of the encapsulated flavor is the same as that of the flavor oil prior to encapsulation. The encapsulated flavors are coarse-grained free-flowing powders consisting of rod-shaped particles, typically with lengths between 0.8 and 1.7 mm and diameters between 100 and 400 μm. The diameter distribution of the flavor droplets, as determined by laser diffraction particle size analysis (Coulter LS 230), varied from 2 to 70 μm with a peak in the distribution at 36 μm. The largely amorphous carbohydrate matrix consisted of a mixture of sucrose (52.8% w/w, dry solids) and maltodextrin (47.2% w/w, dry solids, DE10, Grain Processing Corp.). The maltodextrin was a mixture of maltooligosaccharides with a wide range of degrees of polymerization (DP) typically containing (w/w, manufacturers data) the following: DP1, 0.5%; DP2, 2.7%; DP3, 4.3%; DP4, 3.7%; DP5, 3.1%; DP6, 5.7%; DP7, 7.1%; DP8, 4.5%; DP9, 3.1%; DP10, 1.6%; DP>10, 64.4%. The water contents of the encapsulated flavors were measured using a Karl-Fisher titrator (Baird and Tatlock, model AF5). Samples (100 mg) were first dissolved in 2:1 methanol/formamide (1 mL). Triplicate titrations of 300 μL injections yielded water contents of 3.5% w/w for the encapsulated cherry flavor and 5.2% w/w for the encapsulated peppermint flavor.

The encapsulated cherry flavor was prepared using a model cherry flavor, which comprised benzaldehyde (72% w/w), benzyl alcohol (20% w/w), acetaldehyde (3% w/w), and other minor components including diacetyl, ethyl acetate, ethyl propionate, ethyl butyrate, and ethyl valerate, all present at levels of ~0.5% w/w. The encapsulated peppermint flavor was prepared using a natural peppermint oil, which comprised menthol (52% w/w), menthone (20% w/w), cineole (6% w/w), isomenthone (3.5% w/w), and other relatively minor components at levels of <2% including α- and β-pinene, sabinene, and limonene. The flavor content of the encapsulated products was determined using a modification of the steam distillation method (2.8.12) from the European Pharmacopoeia (1997). Thirty grams of the encapsulated flavor together with 250 mL of distilled water was boiled, and the volume of condensed flavor oil in a graduated section of the receiver arm was monitored until it remained constant over a 30 min period. The flavor content of the encapsulated flavors was calculated from a comparison of the volume, measured after cooling, with the volumes of condensed flavor oil collected when the procedure was repeated with calibration samples of the pure liquid flavor. The linear regression of the volume of oil distilled from the calibration samples gives $R^2 > 0.99$. Using this method, the flavor contents of the encapsulated cherry and peppermint flavors were measured as 10.0 and 7.4% w/w, respectively.

Measurement of Headspace Release of Flavor Volatiles. Gas chromatography (GC) was used to quantify the release of volatile flavor components into the headspace from the encapsulated flavor systems. The effects of the variation of water content and storage temperature on release were analyzed for the cherry samples, and the effect of water content was examined for the peppermint samples. Whereas the volatiles released after a drying or humidification step were measured on the cherry samples, a modified technique, which measured the total volatiles released on humidification, was applied to the peppermint samples. Headspace volatiles were quantified by gas injections onto a Carlo-Erba HRGC5300 GC equipped with a flame ionization detector and a Fisons AS800 autosampler. A BPX5 column (Thames Chromatography), 15 m in length with a 0.32 mm inner diameter and a film thickness of 0.25 μm, was used. The carrier head pressure was 60 kPa, and the injection port and detector temperatures were 240 °C.

Studies on Cherry Samples. For the study of the effect of storage temperature on the release of volatiles from the encapsulated cherry flavor, samples (1.0 g) were weighed into headspace vials (10 mL, chlorobutyl rubber/PTFE seals) and stored at temperatures of 30−100 °C for 3 h and then the headspace volatiles quantified by GC. For the study of the effect of water content on release rate, samples with different water contents were prepared by storing the original material for 24 h at different relative humidities (11−97%) achieved using saturated salt solutions in desiccators (Greenspan, 1977). The water contents of the conditioned samples were calculated from the increase or decrease in the mass of the samples. Triplicate samples (1.0 g) of each material were then sealed into headspace vials (10 mL). The samples were stored at 20 °C for 24 h and examined for the release of flavor volatiles into the headspace by GC. For both experiments the GC oven temperature program was as follows: 60 °C for 3 min, increase temperature to 100 °C at 8 °C/min, increase temperature to

200 °C at 10 °C/min, increase to final temperature of 240 °C at 6 °C/min, and hold for 10 min. For all of the samples a 25 μL injection volume of the headspace was used.

Studies on Peppermint Samples. The water content of the encapsulated peppermint flavor system was varied by sealing samples (0.5 g) into headspace vials (6 mL) together with a holder containing a small amount of water (0−60 μL). There was no direct contact of the liquid water with the encapsulated flavor, and so the water sorbed into the matrix material via the vapor phase. All of the water evaporated from the holders and was absorbed by the matrix material. The samples were then stored at 20 °C for up to 27 days, and the release of volatiles from the samples was analyzed by GC. The GC oven temperature program was as follows: 60 °C for 3 min, increase to 100 °C at 2 °C/min, increase to final temperature of 240 °C at 6 °C/min, and hold for 10 min. An injection volume of 50 μL of the vial headspace gases was used.

Measurement of Hexane Extractable Oil. A sample (2 g) of the encapsulated peppermint flavor was washed with hexane (6 mL) and agitated using an orbital shaker (KS-A Swip, Edmund Bühler) at a shaking rate of 350 min^{-1} for 10 min at room temperature. The sample was filtered under vacuum, the encapsulation product was retained for further washing, and the filtrate was analyzed for flavor components removed in the wash. This procedure was carried out in triplicate. The analysis of the filtrate was carried out using the GC conditions described above (peppermint samples) except for the use of a 0.5 μL liquid injection. The amount of menthone and menthol in each wash was calculated by comparing peak areas of the samples with those of pure calibration samples, and the proportion of extractable oil was calculated using the oil content of the encapsulated flavor given above.

Measurement of Crystalline Sucrose. Fourier transform Raman spectroscopy was used to determine the amount of crystalline sucrose present in stored encapsulation products. A Bio-Rad FT-Raman spectrometer was used to collect the spectra of the samples over the frequency range 100−4000 cm^{-1} with averaging over 200 scans. The data were processed using a partial least-squares (PLS) method with mean centring (Martens and Naes, 1989). A calibration was performed using the spectra of a series of calibration samples containing various proportions of crystalline and amorphous sucrose. The spectra were truncated to a region (1000−1400 cm^{-1}) of the Raman spectrum containing features characteristic of amorphous and crystalline sucrose. The regression method used was PLS. The optimum number of PLS factors was identified as two, at which the prediction error determined by internal cross-validation was minimized and equal to 4 g/100 g. This calibration was used to quantify the amount of crystalline sucrose in experimental samples.

Determination of Glass Transition Temperatures. A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) was used to determine the effect of water content on the glass transition temperature of the largely amorphous carbohydrate encapsulation matrix. The instrument was calibrated for temperature using indium and lead and for enthalpy using indium. The samples (1−2 mg) were weighed accurately using a Mettler balance (model ME30) and hermetically sealed into aluminum DSC pans. The samples were initially scanned from −25 to 70 °C at a rate of 10 °C min^{-1}, then cooled to −25 °C, and rescanned using the same conditions. The glass transition temperatures were determined as the midpoint of the heat capacity increase, which occurs at the glass transition on rescanning the sample.

Scanning Electron Microscopy of the Encapsulated Flavors. Samples of the encapsulated flavors were mounted by sprinkling the rods onto self-adhesive pads on aluminum pin stubs (Agar Scientific). The specimens were sputter coated (5 min) with a layer of gold (~25 nm thick) using an Emitech K550 sputter coating unit. The specimens were examined in a Leica-Cambridge Stereoscan 360 scanning electron microscope at an accelerating voltage of 10 kV. The images were viewed within 1 h of entering the microscope vacuum chamber.

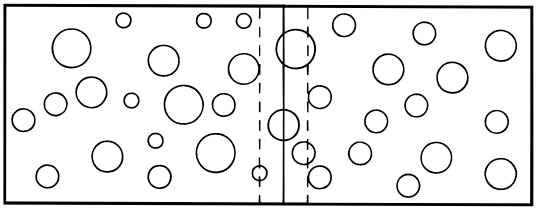

Figure 1. Section through the axis of a cylindrical rod of encapsulated flavor. Circles represent flavor droplets. Solid vertical line through center represents the fracture. Dashed lines, a distance $d_i/2$ from the fracture, enclose the centers of the droplets, diameter d_i, which will be exposed to the headspace by the fracture.

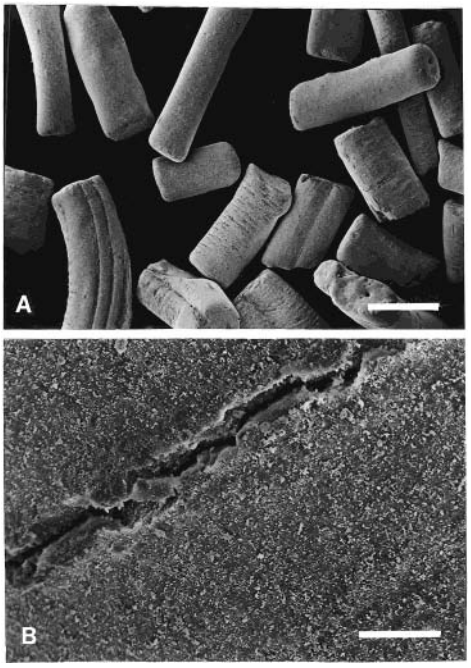

Figure 2. (A) Micrograph of rods of encapsulated cherry flavor. Length bar = 0.5 mm. (B) Micrograph of crack in rod of encapsulated cherry flavor. Length bar = 20 μm.

Model To Estimate Volume Fraction of Flavor Oil Exposed to the Headspace by Fracture or Cracking. A section through a cylindrical rod of encapsulated flavor is shown in Figure 1. The spherical flavor droplets have a distribution of diameters with a volume fraction ϕ_{di} in the diameter range d_i to $d_i + \Delta d_i$. ϕ_e is the volume fraction of flavor exposed to the headspace due to a fracture with area A. If the center of a droplet is within a radius of the fracture surface, then it will be exposed to the headspace. The fraction of droplets exposed depends on the fraction of the total volume enclosed by the dashed lines in Figure 1. The volume fraction of droplets in the diameter range exposed is $Ad_i\phi_{d_i}/V$, where V is the volume of the rod. Summed over all diameters, this yields $\phi_e = A\sum d_i\phi_{d_i}/V$. The summation $\sum d_i\phi_{d_i}$ depends on the normalized size distribution and the volume fraction of the flavor droplets, $\phi = 0.13$. The summation was performed for the encapsulated cherry flavor, yielding $\sum d_i\phi_{d_i} = 2.3$ μm.

RESULTS

Figure 2A shows an electron micrograph of the encapsulated cherry flavor. The samples show some heterogeneity in terms of rod diameters, lengths, surface textures, and the occurrence of some pairs of rods fused together. Whereas the majority of the rods viewed were free from cracks, a minority (~10%) showed some limited surface cracking. One of the rods to the right of center in Figure 2A shows some cracking. Figure 2B

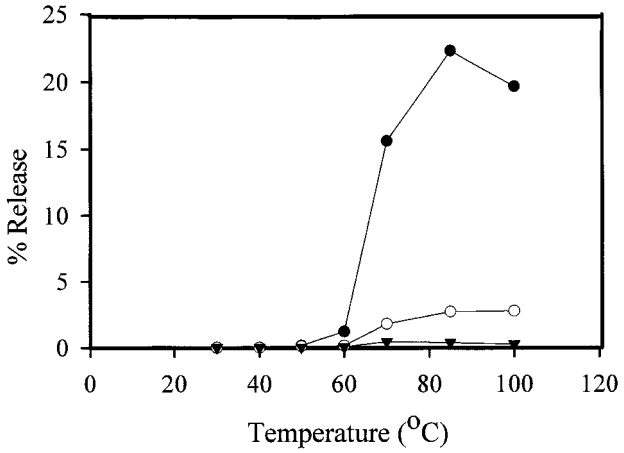

Figure 3. Effect of storage temperature on the headspace release of flavor volatiles from the encapsulated cherry flavor. Volatiles: (●) acetaldehyde; (○) benzaldehyde, release × 10; (▼) benzyl alcohol, release × 10.

shows this crack at higher magnification; at the surface it is ~5 μm wide, narrowing to ~1 μm deeper into the specimen. The encapsulated peppermint flavor showed the same features.

Figure 3 shows the effect of storage temperature on the headspace release of flavor components (acetaldehyde, benzaldehyde, and benzyl alcohol) from the encapsulated cherry flavor (water content, "as prepared" = 3.5% w/w). The percentage release for these studies is expressed as the amount of the volatile in the headspace as a percentage of the total amount of that volatile originally in the sample. For storage temperatures up to 50 °C the level of release of each component of the encapsulated cherry flavor was relatively low, with acetaldehyde, the species with the highest release, at <0.2%. For the two main components, benzaldehyde and benzyl alcohol, the level was actually <0.015%. However, as the storage temperature was increased to 60 °C and above, the percentage release of each of the flavor components in the headspace increases. The release of benzaldehyde and benzyl alcohol reached ~0.3 and ~0.03%, respectively, at a storage temperature of 100 °C, and the corresponding release of acetaldehyde was higher, reaching ~20% at 90−100 °C.

The effect of water content on the headspace release of flavor components from the encapsulated cherry flavor is shown in Figure 4. At a water content of 3.5% w/w, the water content of the system after its preparation, the lowest levels of each of the cherry flavor components were present in the headspace (<0.04% acetaldehyde and <0.001% benzaldehyde and benzyl alcohol). As the matrix water content was increased, the levels of all the flavor components observed in the headspace increased. At small water additions the release increased linearly, but at water contents of ~5.2% w/w for the acetaldehyde and ~6.7% w/w for the benzaldehyde, there was a large increase in the rate of release. At the highest water contents studied (8−9% w/w), the release of acetaldehyde was again much greater than that of the two main components of the flavor, benzaldehyde and benzyl alcohol. The percentage release of acetaldehyde reached levels of up to 8%, whereas the levels of benzaldehyde and benzyl alcohol were 0.3 and 0.04%. It should be noted that, depending upon the release rates during conditioning, the water content may have been underestimated. At the higher water contents (>6.8% w/w) total volatile release reached

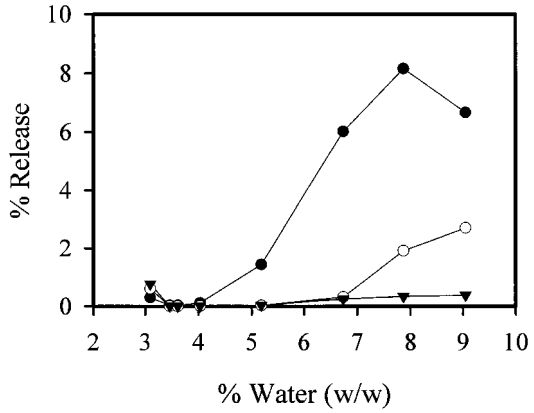

Figure 4. Effect of water content on the headspace release of flavor volatiles from the encapsulated cherry flavor. Volatiles: (●) acetaldehyde; (○) benzaldehyde, release × 10; (▼) benzyl alcohol, release × 10.

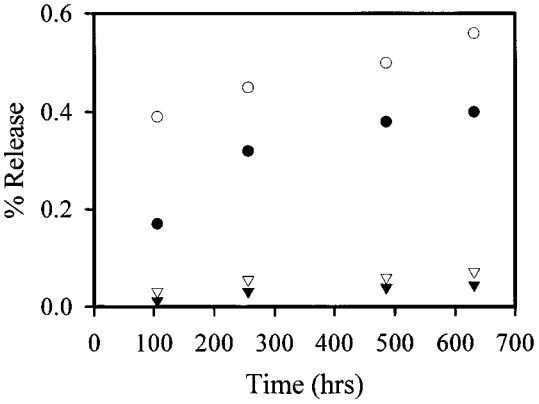

Figure 5. Effect of water content on the headspace release of volatiles from the encapsulated peppermint flavor. Volatiles: cineole with 10.9% water (●) or 13.7% water (○); menthone with 10.9% water (▼) or 13.7% water (▽).

0.09% w/w; it is under these conditions that volatile release during conditioning may have affected estimates of water content which were calculated by weight change. Figure 4 also shows release data under conditions when the water content is reduced below the "as prepared" water content of 3.5% w/w. With a reduction in water content of 0.5% w/w there was an increased release of all the components into the headspace. There was ~10 times as much acetaldehyde in the headspace, as compared with the "as prepared" material, and >50 times as much benzaldehyde and benzyl alcohol.

A time-resolved study of the effect of water content on the release of flavor components was carried out on the encapsulated peppermint flavor system. Samples with a range of water contents were prepared in sealed headspace vials and stored for 4 weeks at 20 °C. Figure 5 shows the evolution of release of cineole and menthone into the headspace with increasing storage time at water contents of 10.9 and 13.7% w/w. Systems with lower water contents (between 5.4 and 9.0% w/w) showed no measurable release of the main components of the peppermint oil over the studied period, and the major component, menthol, was not observed in the headspace of any of the samples. The release of cineole and menthone into the headspace was observed to increase with increasing water content, as for the cherry matrix (see Figure 4). Headspace release increases relatively rapidly in the first 100 h followed by a period of slowly increasing release. After nearly 4 weeks at 20

Table 1. Amount of Menthone and Menthol Washed from Encapsulated Peppermint Flavor by Successive Hexane Washes[a]

	% of total	
wash	menthone	menthol
1	0.05 ± 0.01	0.23 ± 0.03
2	0.09 ± 0.02	0.17 ± 0.02
3	0.12 ± 0.04	0.13 ± 0.02
overall	0.26 ± 0.07	0.53 ± 0.07

[a] Range of values measured for triplicate measurements given.

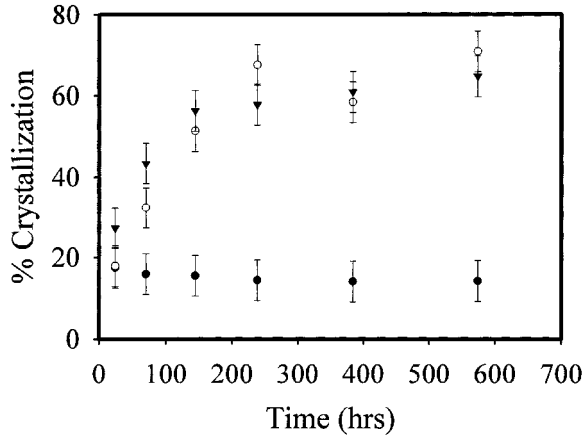

Figure 6. Effect of water content on sucrose crystallization in the matrix of encapsulated peppermint flavor. Water contents: (●) 8.8%; (○) 11.5%; (▼) 14.1%.

°C, the cineole reached levels of about 0.4 and 0.6% for matrix water contents of 10.9 and 13.7% w/w, respectively, and the menthone was present at levels of about 0.04 and 0.07% for the same matrix water contents.

Table 1 shows the amounts of menthone and menthol extracted from the encapsulated peppermint flavor during three successive hexane washes. The levels of each component washed from the rods was very small, up to 0.14% for menthone and up to 0.26% for menthol.

Fourier transform Raman spectroscopy was used to identify and quantify the physical state of the sucrose in the carbohydrate matrix, that is, whether it is present in an amorphous state, mixed with the maltooligosaccharides of the maltodextrin, or in a crystalline state having crystallized during storage. Figure 6 shows the percentage of crystalline sucrose, as measured by Fourier transform Raman spectroscopy, as a function of the storage time at 20 °C for the encapsulated peppermint flavor system containing different amounts of water. At the highest water contents studied (11.5 and 14.1% w/w) the crystallinity of the sucrose increased with storage time. The crystallinity increased steadily over the first 200 h of storage and then leveled off at a sucrose crystallinity of ~70%. At lower water contents (≤8.8% w/w), no change in the crystallinity of the sucrose was detected after the first measurement in the storage experiment.

Figure 7 shows the glass transition temperatures of the carbohydrate matrixes of the encapsulated cherry and peppermint flavors as a function of the water content of the system. With increasing water content there is a decrease in the observed glass transition temperature (T_g) of the carbohydrate matrix. The addition of water to the "as prepared" encapsulation matrix leads to plasticisation of the matrix and a

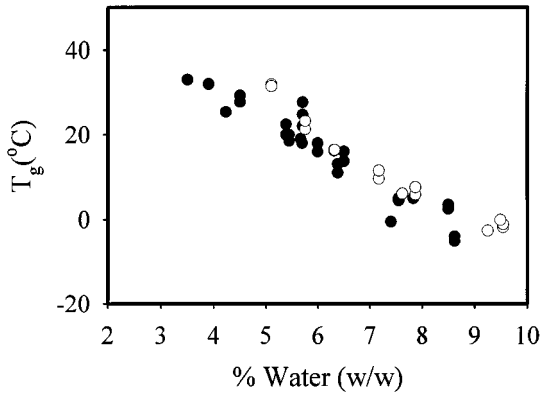

Figure 7. Effect of water content on the glass transition temperature of matrixes of the encapsulated cherry (●) and peppermint (○) flavors.

depression of the observed T_g (Levine and Slade, 1986; Orford et al., 1989).

DISCUSSION

One aim of this study was to understand the mechanisms by which encapsulated flavors are released from low water content carbohydrate matrixes. It was hypothesized that the matrixes would be permeable to at least some of the flavor components; for example, in the cherry flavor, acetaldehyde is a small molecule that might be expected to be mobile in the carbohydrate matrix, its carbonyl group giving it sufficient polarity to partition into the matrix and so be able to diffuse through the matrix in a manner analogous to water (Parker and Ring, 1995). Prior to discussing matrix permeability, it is necessary to consider what levels of release occur from any flavor oil with direct access to the headspace. This would include any surface oil and any oil with access to the surface as a result of the fracture of rods or cracking of the matrix. The electron micrographs show some limited cracking of the rods, and by using a simple geometrical model, it is possible to estimate the order of magnitude of the release that results from cracks and fractures. To estimate ϕ_e, it is necessary to first estimate A/V, the ratio of the crack or fracture area to the volume. Taking typical dimensions (rod diameter = 250 μm; length = 1200 μm; 10 μm deep crack around circumference) and number of cracks (10% of rods cracked) yields $A/V = 1.3 \times 10^{-5}$ μm^{-1}. This gives a release $\phi_e/\phi = 0.023\%$. This is of the same order of release observed for acetaldehyde from the "as prepared" material in the temperature and water content studies of the encapsulated cherry flavor. On the basis of this calculation it can be concluded that the release from the "as prepared" materials could originate from flavor oil with direct access to the headspace. Further evidence that the release from the "as prepared" materials is by direct access rather than matrix permeability can be inferred from Figure 3 by the following argument. In the absence of the encapsulating matrix the flavor volatiles would simply evaporate into the headspace until saturation was achieved and an equilibrium headspace concentration was reached (The total amount of flavor in the headspace vials is such that complete evaporation does not occur.) Considering the data in Figure 3, at high temperatures (80−100 °C) ~20% of all the acetaldehyde is able to diffuse into the headspace. This means that the equilibrium headspace concentration, which would be obtained when

acetaldehyde has free access to the headspace, corresponds to a release of at least 20% and possibly more. However, at temperatures <50 °C, <0.2% is released, a factor of 100 lower than the high-temperature value. The sharp increase in headspace concentration over the interval 50−80 °C is greater than would be expected from changes in matrix permeability and the solubility of acetaldehyde in the cherry flavor, and so we argue that release mechanisms other than matrix permeability must be dominant. Because matrix permeability to a particular component is the product of the diffusivity and its partition coefficient between the flavor and matrix phases, either, or both, of these factors could be leading to the low permeability. Furthermore, the occurrence of headspace release of acetaldehyde is correlated with the release of benzaldehyde and benzyl alcohol, species with limited polarity, which would be expected to have negligible solubility in the matrix. Le Thanh et al. (1992) found little sorption of benzaldehyde by low water content maltodextrins. Benzaldehyde and benzyl alcohol can only be released if they have a direct path to access the headspace. Possible mechanisms by which these species can access the headspace include evaporation of surface (unencapsulated) flavor oil, subsurface flavor oil droplets breaking through to the surface of the matrix, and fracture or cracking of the solid matrix exposing droplets from the interior of the matrix particles. The presence of benzaldehyde and benzyl alcohol in the headspace at temperatures close to ambient indicates that small amounts of flavor oil are present, which can simply evaporate into the headspace without any release from the matrix being necessary. Qualitatively, low levels of acetaldehyde in the headspace over samples at temperatures close to ambient could also originate from the same sources without the need to invoke matrix permeability. A knowledge of the permeability of the matrix to acetaldehyde would be required to substantiate that release by this mechanism is relatively slow.

Quantifying the amount of oil accessible from the surface by solvent is complicated by the fact that agitation involved in washing the flavor oil from the rods appears to result in further release. Table 1 shows that the total quantities of menthone and menthol which can be washed from the encapsulated peppermint flavor system using hexane amount to 0.26 and 0.53%, respectively. These amounts exceed the amounts observed in the headspace under conditions when release was observed (Figure 5). The amounts of menthone and menthol observed in the washes are sufficient to saturate the headspace of the "as prepared" material; however, this was not observed experimentally, and it must be concluded that the washing process is itself causing the release. The amounts of oil that evaporate into the headspace of the "as prepared" material are considerably lower than the amounts which can be washed from the product. Recently Minemoto et al. (1997) found that the amount of lipid extracted from polysaccharide-based (gum arabic) microcapsules using chloroform increased with extraction time. They reported that surface oil was removed in the first 3−20 s, depending upon the mode of preparation (microstructure) of the microcapsules. Moreau and Rosenberg (1993) reported similar experiences in their studies of the extractability of anhydrous milk fat with petroleum ether from whey protein and whey protein−lactose-based microcapsules. These studies show some similarities, although the different solvents, walls, and encapsulated materials should be noted. Clearly, care is needed in developing liquid washing techniques for quantifying the amount of surface accessible flavor oils.

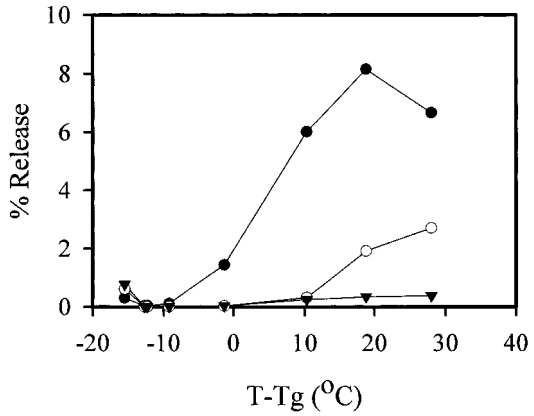

Figure 8. Effect of water content on the headspace release of flavor volatiles from the encapsulated cherry flavor, expressed in terms of the temperature interval above the glass transition temperature, $T - T_g$. Volatiles: (●) acetaldehyde; (○) benzaldehyde, release × 10; (▼) benzyl alcohol, release × 10.

The crystallization of the sucrose in the matrix (Figure 6) correlates with release (Figure 5). Similar relationships have previously been reported for the release of methyl linoleate from lactose-based matrixes (Shimada et al., 1991; Labrousse et al., 1992) and of propanol from sucrose-based matrixes (Levi and Karel, 1995) and for the extractability (by solvent) of anhydrous milk fat from lactose-based matrixes (Moreau and Rosenberg, 1993). Furthermore, the occurrence of crystallization and release also correlates with the storage of the sample in its supercooled liquid state at temperatures above its glass transition temperature (Figure 7). These observations are related as the nucleation and growth of sucrose crystals in amorphous mixtures can be related to the extent to which storage temperature exceeds the glass transition temperature, $T - T_g$ (Kristott and Jones, 1992; Kedward et al., 1998). In particular, the glass transition temperature of the matrix of the peppermint flavor systems is below −10 °C at water contents of 11.5 and 14.1% w/w (Figure 7), and so at 20 °C the matrixes of these samples (Figure 6) are at least 30 °C above their glass transition temperatures. In these systems sucrose crystallization proceeds to ∼70% over 200 h, and release of cineole and menthone into the headspace proceeds over a similar time scale (Figure 5). The sample with 8.8% w/w water (Figure 6) shows a limited crystallization, its glass transition temperature is ∼−3 °C, and so it is being stored at a temperature that is 23 °C above its glass transition temperature. Peppermint samples stored under these conditions showed no measurable release. Using the glass transition temperature−water content relationship in Figure 7 (with some extrapolation at high water contents), the release data in Figure 4 can be replotted in terms of $T - T_g$, the temperature interval by which the storage temperature exceeds the glass transition temperature (Figure 8). In this case the increase in release of the acetaldehyde appears at about T_g and the increase in release of benzaldehyde and benzyl alcohol at about $T - T_g$ of 10 °C. In these experiments release is occurring at storage temperatures much closer to T_g. This may indicate that the transformation of the matrix from glassy solid to highly

viscous liquid is sufficient to allow some flavor droplets breaking through to the surface of the matrix. During water sorption water content and local glass transitions will vary throughout the material, depending upon how quickly water is taken up by and diffuses through the material. The T_g values discussed above are effectively mean values for a homogeneous material. During water sorption the glass transition temperature of surface layers will have dipped below this mean value. Thus, although acetaldehyde release appears to be occurring at about T_g, the surface layers from which release occurs will have experienced lower glass transition temperatures and a correspondingly lower viscosity.

Further work is needed to understand why sucrose crystallization results in release. The effects of increasing the concentration of the flavor emulsion and liquefaction of the amorphous portions of the matrix as water is expelled from the domain of the growing sucrose crystals must result in a proportion of the flavor oil gaining access to the surface of the matrix and evaporating into the headspace.

CONCLUSIONS

In these experiments no evidence was found for the sucrose−maltodextrin matrix being permeable to any of the flavor components. The release of all the flavor components followed essentially the same pattern. The largest amount of release occurred when the matrix was in a supercooled liquid state, above its glass transition temperature, under conditions when the sucrose in the matrix crystallized. Smaller amounts of release were observed when the water content of the matrix was lowered while in its glassy state. Even smaller amounts of release occurred in the "as prepared" state, which were assigned to evaporation of the small amounts of flavor oil with access to the headspace. Surface oil is difficult to quantify as even mechanically gentle washing procedures extract more oil than evaporates into the headspace.

The occurrence of a fraction of the flavor oil (surface oil and subsurface oil in cracks) which can release small amounts of flavor into the headspace means that low levels of leakage of encapsulated flavor due to diffusion through the matrix cannot be distinguished. Single-phase mixtures are probably required to unambiguously observe matrix permeability. The release mechanisms presented in this paper are distinct from those proposed previously for volatile retention during drying processes (Flink and Karel, 1970; Thijssen, 1971) in that the two-phase nature of the flavor emulsion is recognized with negligible amounts of flavor partitioning into the low water content matrix.

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