*ASEAN Food Journal 14 (1): 1-14 (2007)*

**Review Paper**

# Microencapsulation of Vitamins

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## INTRODUCTION

Functional foods are beginning to play a major role in what consumers buy and eat. The International Life Science Institute has defined a functional food as 'a food which has a beneficial effect on one or more target functions of the body, above and beyond the usual effects of food, such as improving the state of health and well-being or reducing the risk of disease. Examples of these types of food include folate addition to breakfast cereals to reduce the risk of neural tube defects in the developing fetus, milk fortification with calcium to combat osteoporosis and addition of omega 3 to breads to aid in reducing heart disease. Currently, health claims are illegal on food packaging in Australia (except for claims relating to folate). Food Standards Australia and New Zealand are reviewing this legislation to allow general health claims by mid 2006 (Herald Sun, 27/05/05).

Some nutrients do not remain in the food for a significant amount of time or may react with the other food components causing undesirable effects. Microencapsulation is a technology that can improve the retention time of the nutrient in the food and allow controlled release at specific times, during food consumption or in the intestinal gut. It is not a new technology and was first commercially applied in 1954 for carbonless copy paper (Dziezak, 1988). Microencapsulation technique has been utilised in the pharmaceutical industry for the past 30 years to offer controlled release of drugs to the body (Rosinski *et al.*, 2002). It is relatively new to the food industry and is finding use in maximising the retention of the bioactivity of the components during the processing and storage of the formulated product and delivering the desired bioactive components to the target site of the body (Korhonen, 2002). Microencapsulation has been used to encapsulate fish oil to increase n-3 polyunsaturated fatty acid intake (Higgins *et al.*, 1999), to encapsulate probiotic bacteria in frozen dairy foods (Shah and Ravula, 2000) and among other things, to encapsulate 2-acetyl-1-pyrroline (ACPY; a major flavour component of aromatic rice) to retain this flavour component upon storage (Apintanapong and Noomhorn, 2003).

## MICROENCAPSULATION

Microencapsulation is the creation of a barrier to avoid chemical reactions and/or to enable the controlled release of the ingredients (Vilstrup, 2001). It involves mass transport behaviour in some way between the core (the ingredient) and the shell (capsule or coating). The entrapped material is usually a liquid but may be a solid or a gas. Table 1 outlines the reasons why the food industry applies microencapsulation.

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**Table 1:** Reasons why the food industry applies microencapsulation

1. To reduce the reactivity of the core in relation to the outside environment (eg, light, oxygen and water)

2. To decrease evaporation rate of the core material to the outside environment.

3. To promote easier handling of the core material to:
   - prevent lumping
   - give a uniform position of the core material
   - convert a liquid to a solid form
   - promote easy mixing of the core material.

4. Control the release of the core material to achieve the proper delay for the right stimulus.

5. To mask the core taste.

6. To dilute the core material when it is used in only small amount but still achieve uniform distribution.

Adapted from Shahidi and Han (1993).

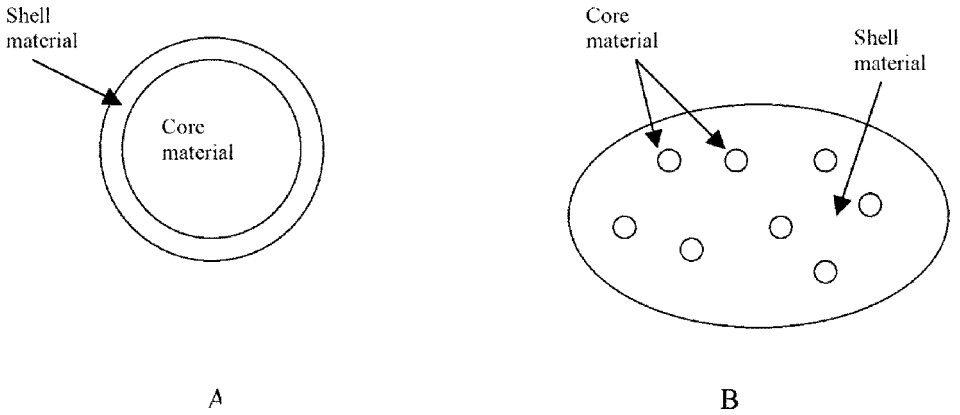


**Figure 1**: Diagram of two representations of microcapsules: (A) continuous core surrounded by continuous shell; (B) core material dispersed in a matrix of shell material

The capsule is very small in size, approximately 5 – 300 micron in diameter (Gibbs *et al.*, 1999). It can consist of a continuous core region surrounded by a continuous shell or it can have irregular geometry consisting of small particles of core material dispersed in a matrix of shell material (Vilstrup, 2001). This is shown by a schematic diagram in Figure 1. Generally a hydrophobic core is usually protected by a hydrophilic shell, and hydrophilic material is protected by a hydrophobic shell. The shell can consist of one or more materials. The shell of the capsule is designed to prevent diffusion of the core material into the food until the desired time. Its functions involve protecting sensitive food components such as flavours, vitamins or salts from water, oxygen or light, converting liquids that are difficult to handle into free flowing powders, and isolating specific food

**Table 2:** Approved food grade capsule shell material (Vilstrup, 2001)

| Polysaccharides | Fats and waxes | Proteins |
|---|---|---|
| Gum Arabic | Hydrogenated vegetable oils | Gelatins (types A and B) |
| Modified starches | Bees wax | Whey proteins |
| Hydrolysed starches (maltodextrins) | Soy proteins | |
| Alginates | | Sodium caseinates |
| Pectin | | |
| Carrageenan | | |

components from other food components during storage.

***Capsule Material***

There are a number of commercially approved shell materials available to produce various microencapsulated foods. Table 2 outlines approved food-grade capsule materials. Not all shell materials meet all the properties needed, so they are often used in combination with other coating materials with other modifiers such as oxygen scavengers, antioxidants, chelating agents and surfactants (Shahidi and Han, 1993). Carbohydrates such as starch and cyclodextrins have good ability to absorb volatiles from the environment. This makes them good for flavour encapsulation. Gum Arabic is a commonly used capsule material due to its viscosity, solubility and emulsification characteristics but its cost is a major disadvantage. Alginates and hydrocolloids are extracted from kelp and react with calcium ions to form a stable gel. They can then be used to entrap flavour oils at ambient temperatures.

Protein based materials are able to form stable emulsions with volatile flavour components but their solubilities in cold water, potential to react with carbonyls and high cost limit their application. Ethyl cellulose is a good material to encapsulate water soluble vitamins because it is water soluble itself and as the shell thickness increases, the water permeability of the core vitamin is reduced (Shahidi and Han, 1993).

***Release Mechanisms***

Some microencapsulated materials are made for controlled release of the microencapsulant, perhaps during processing, storage or during final preparation prior to consumption. Food additives which may benefit from controlled release capsules include preservatives, redox agents, colours, sweeteners and enzymes. Commonly used methods for controlled release in foods include temperature and moisture release for hydrophilic encapsulants, and thermal release for fat capsules (Risch and Reineccius, 1995). Other release methods include pH control, addition of surfactants, enzymatic release, ultrasonics, grinding, and photo-release.

## MANUFACTURING TECHNIQUES

There are numerous methods for micro-encapsulation of food ingredients but no single encapsulation process is adaptable to all core materials or product applications. Table 3 outlines common methods used to encapsulate food ingredients.

Three steps are generally involved including formation of the wall around the material, ensuring that leakage does not occur, and ensuring that undesired materials are kept out.

***Spray Drying***

Spray drying is the most common methods used for microencapsulation because it is economical. It is also one of the oldest

**Table 3:** Methods for encapsulating food ingredients

| Encapsulating method | Food ingredients |
|---|---|
| Spray drying | Vitamins, flavours, starter cultures carotenoids, fats and oils, clouding agents. |
| Spray cooling and spray chilling | Ferrous sulphate, vitamins, minerals, acidulents. |
| Extrusion | Vitamin C, visible flavour pieces, colours and extension of shelf life. |
| Fluidised bed coating | Vitamin C, citric acid, lactic acid, sorbic acid, sodium bicarbonate in baked goods. |
| Liposome entrapment | Delivery of vaccines, hormones, enzymes and vitamins in to the body. |
| Coacervation | Vitamin A |

encapsulation methods used originally in the 1930's to encapsulate flavours using gum acacia (Shahidi and Han, 1993). The basic steps involved in spray drying include preparation of the dispersion or emulsion to be processed, homogenisation of the dispersion, and atomisation of the mass into the drying chamber.

The materials used for the capsule are food grade hydrocolloids such as modified starch, maltodextrin and gums (Gibbs *et al.*, 1999). The material should have good emulsifying properties, be a good film former, have low viscosity and provide good protection to the encapsulated ingredient.

The carrier is hydrated in water. The ingredient to be encapsulated is added to the carrier and homogenised. An emulsifier may also be added at this stage. The ratio of encapsulant to carrier is usually 1:4 (Gibbs *et al.*, 1999) but this can be optimised for each individual ingredient. This mixture is then fed into the spray dryer and atomised with a nozzle or spinning wheel. Water is evaporated by the hot air (100-160$^{o}$C) and the small particles are deposited to the bottom of the spray dryer where they are collected. The air temperature can be optimised to produce the maximum retention of encapsulant. Dib Taxi *et al.* (2003) studied the microencapsulation of camu-camu juice. It is a fruit from the Amazon with high vitamin C content. The optimum conditions for juice yield and vitamin C retention were established with 15% wall material and air entry temperature of 150$^{o}$C. Uddin *et al.* (2001) found that the loss of ascorbic acid during encapsulation by spray drying was only 2%.

***Spray Chilling and Spray Cooling***

It is a challenge to encapsulate water-soluble food ingredients for protection during the shelf life of the food. It is often difficult to find a good food grade barrier that will prevent leaching of its water into the food. Spray chilling and cooling are ideal methods for such cheeses. Schrooyen *et al.* (2001) encapsulated vitamin C for applications in solid foods such as cereal bars, biscuits and bread. The methods are similar to spray drying in that they disperse a core material into a liquified coating and then atomised. However, the air temperature is cooler than that for spray drying, and ambient temperatures are used for spray cooling and refrigeration temperature for spray chilling. The wall material is a molten fat or wax. Spray cooling uses a vegetable oil with a melting point in the range of 45-122$^{o}$C. Spray chilling uses a fractionated or hydrogenated vegetable oil with a melting point in the range of 32-42$^{o}$C (Risch and Reineccius, 1995). The microcapsules produced are insoluble in water due to the lipid coatings.

Frozen liquids, heat-sensitive materials and those not soluble in the usual solvents can be

encapsulated by spray chilling. Applications can include dry soup mixes, foods with high fat contents and bakery products (Gibbs *et al*., 1999).

***Extrusion***

This method was first patented in 1957. The advantage of extrusion is that it completely surrounds the core material with wall material. It is a true encapsulation method. The process involves forcing a core material dispersed in a molten carbohydrate mass through a series of dies, into a bath of dehydrating liquid. When contact with the liquid is made, the carbohydrate case hardens to entrap the core material. The extruded filaments are separated from the liquid bath, dried using an anti-caking agent such as calcium tripoly-phosphate and sized (Shahidi and Han, 1993). This process is particularly useful for heat labile substances such as flavours, vitamin C and colours. Encapsulated flavours have applications in drink mixes, cake mixes, gelatin dessert mixes and cocktail mixes (Dziezak, 1988).

***Fluidised Bed Coating***

This process is also known as air suspension coating. It is accomplished by suspending solid particles of the core material in an upward moving stream of air, which can be heated or cooled. Once this 'fluid' bed of particles has reached the required temperature, it is sprayed from the top by atomised particles of coating wall material. This wall material can be either in a molten state or dissolved in an evaporable solvent. The molten coating is hardened by solidification in cold air. The solvent-based coating is hardened by evaporation of the solvent using hot air (Risch and Reineccius, 1995). The coating can be selected from cellulose derivatives, dextrins, emulsifiers, lipids, protein derivatives and starch derivatives (Shahidi and Han, 1993). A thin layer of coating is deposited onto the core material and full coverage is achieved by multiple passes through the air stream. Optimum encapsulation results are obtained with core particle sizes of between 50 and 500 microns (Gibbs *et al*., 1999).

The two most important processing variables in this process are volume of fluidised air used, which controls the height of the substrate particles in the air stream and determines their surface coating time. The other variable is air temperature. This is a critical factor as improper temperature control will result in incomplete coverage by the coating material and thus lead to a poor quality product (Risch and Reineccius, 1995).

This method is common for use in the nutritional supplement market to supply encapsulated versions of vitamin C, vitamin Bs, ferrous sulphate, ferrous fumarate, sodium ascorbate, potassium chloride and a variety of vitamin / mineral premixes. It has applications in baked goods, seasonings, fillings, desserts and dry mix puddings (Risch and Reineccius, 1995).

***Liposome Entrapment***

Liposomes are single or multi-layered vesicles, which involve the complete enclosure of an aqueous phase within a phospholipid-based membrane. These vesicles form spontaneously when phospholipids are dispersed in an aqueous media (Risch and Reineccius, 1995). The phospholipids make up the outer layer of the liposomes, as shown in Figure 2. The hydrophilic portions are positioned towards the aqueous phase and the hydrophobic groups associate with the hydrophobic ones of other lipid molecules. It forms a sheet which when folded into a spherical shape, results in a very stable capsule. Aqueous or lipid-soluble materials, but not both, are entrapped in these membranes and this forms the basis of encapsulation. Flavour compounds are commonly encapsulated using this method. Kirby *et al*. (1991) used this material to encapsulate ascorbic acid with high efficiency and a very stable material.

Liposomes can be made in sizes ranging from a few nanometers to several microns (Risch and Reineccius, 1995). The most stable liposomes are made from lecithin, cholesterol

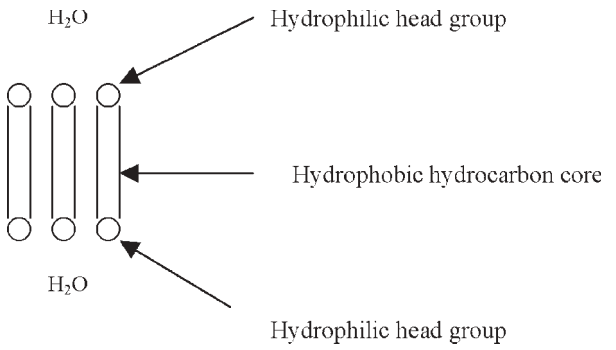


**Figure 2**: Schematic diagram of lipid bilayer

and negatively charged phospholipid. A common method for the manufacture of liposomes is by the dehydration-rehydration method so long as no organic solvents are used. It results in the fusion of adjacent vesicles and entrapment of the associated solute in the multilayered liposomes.

***Coacervation***

The coacervation process is also known as phase separation. It was developed in the 1950's as a means of providing a two ink system for carbonless copy paper (Shahidi and Han, 1993). Particle sizes of a few submicrons to a centimetre are obtained (Gibbs *et al*., 1999). This has only recently been used for food grade encapsulation and is a very expensive process. It is efficient, but is limited by the lack of suitable encapsulating materials approved for food (Shahidi and Han, 1993).

Coacervation involves the separation of a liquid phase of coating material from a polymeric solution and the wrapping of that phase as a uniform layer around the suspended core particles (Dziezak, 1988). It consists of dissolving gelling protein, followed by emulsification of the core material into the protein. The liquid coating is removed from the polymer solution and is then used to coat the material to be encapsulated by controlled physical mixing. It is solidified by either thermal, cross-linking or de-solvation techniques. The microcapsules are collected by centrifugation or filtration, washed with an appropriate solvent and dried by spray drying or fluidised bed drying. The results are free-flowing and discrete particles.

Coacervation occurs either through a simple or complex method. Simple coacervation involves only one colloidal solute such as gelatin whereas complex coacervation involves the use of a second oppositely charged hydrophilic colloid such as gelatin and gum acacia or gelatin and polysaccharide (Gibbs *et al.*, 1999). Hydrophilic coatings such as gelatin can be used to microencapsulate hydrophobic substances including citrus or vegetable oils or vitamin A (Gibbs *et al.*, 1999). Junyaprasert *et al*. (2001) studied the effect of process variables on the microencapsulation of vitamin A palmitate by complex coacervation using gelatin and acacia.

## MICROENCAPSULATION OF VITAMIN C

Vitamin C (ascorbic acid) is a water-soluble vitamin. It is common in fruits and vegetables such as guava, orange, capsicum, apple, pawpaw, brussel sprout, strawberry, kiwi fruit and cauliflower. It is essential for the manufacture of collagen protein, wound

healing, healthy immune and nervous systems and as an antioxidant to help prevent diseases (Reavley, 1998).

It is stable as a powder but this stability decreases when dissolved in water. Environmental factors such as temperature, pH, oxygen, metal ion, UV and x-ray affect the stability (Uddin *et al.*, 2001). Ascorbic acid is highly oxidative which can cause a problem in food systems. In the processing stage, it can change colour from white to yellow which affects food colours. Also, it can react with other ingredients and bring about undesirable changes in the colour and taste of the food.

The pH value of the food affects the ascorbic acid as the oxidation rate of ascorbic acid is maximum at pH 5.0 and 11.5. UV and x-ray irradiation causes a free-radical photochemical oxidation under both aerobic and anaerobic conditions (Davies *et al.*, 1991). However, it is this oxidative effect that makes vitamin C such a good antioxidant.

A healthy diet and consumption of a variety of foods should ensure adequate supply of vitamin C to the body. However, in today's society this is not always the case. Nutrient supplements are extremely popular and there is a growing interest in fortification of foods. Stable vitamin C would be a good asset to fortify foods. Microencapsulation can help to stabilise vitamin C. Many studies have been done on this vitamin with variables optimised to determine the most stable way of microencapsulating vitamin C to give the highest retention possible and to use these applications in food fortification.

Uddin *et al.* (2001) studied the effect of process variables on ascorbic acid characteristics. They chose four different encapsulation techniques – thermal phase separation, melt dispersion, solvent evaporation and spray drying. The thermal phase separation technique used ethyl cellulose as the wall forming material. Its molecular weight was varied and other parameters remained the same. It was determined that microencapsulation product size decreased as the molecular weight increased. The most probable reason given for this was the decrease in the aggregation of the microcapsules as the molecular weight of ethyl cellulose increased. They also studied the release rate of ascorbic acid, which is defined as the ratio of ascorbic acid released to the solution to its initial encapsulated weight. This was determined by suspending 200 mg of microcapsules in 1000 ml of water and continuous shaking at 30°C. The amount of ascorbic acid released was quantified using a UV spectrophotometer. Results show that there is a significant difference in release ratios with different molecular weights of ethyl cellulose. The higher the molecular weight, the lower is the initial release rate. Molecular rate was not a factor for complete release as high or low molecular weight gave a release rate of ~1.0 in 20 minutes. This compares favourably to free ascorbic acid, which achieved a release ratio of 1.0 after only 20 seconds of dissolution.

Carnauba wax was used in the melt dispersion method of microencapsulation. Results show spherical microcapsules of approximately 50 $\mu$m in size. The release ratio was almost 0.6 after 120 minutes which is substantially lower and slower than using ethyl cellulose in phase separation. This shows that carnauba wax keeps the ascorbic acid more stable.

The solvent evaporation technique was used to investigate effects of varying temperature, core-to-wall ratio and the presence of plasticisers (triethyl citrate) on the microencapsulated ascorbic acid. Results showed that the presence of plasticiser decreased the release rate. Two core-to-wall ratios used were 1:1 and 3:1. No significant effect was found. Similarly, the two temperatures used for solvent evaporation of 28°C and 55°C, showed no significant effect on the release rate.

The spray drying technique used four different polymer-coating materials, whether singly or as a mixture. They were gel, starch, ethyl cellulose and $\beta$-cyclodextrin. The results showed that ascorbic acid loss during spray

drying was only 20% which is considered low. Each of the various coating materials resulted in capsule sizes mostly between the 90-280$^{o}$ m fractions. However, the encapsulated ratio of ascorbic acid was not very high, less than 50%. This means that less than 50% of ascorbic acid used in the technique was actually microencapsulated. While spray drying is a cheap and economical method of encapsulation, this value is not very high. The encapsulated ratio was slightly higher when $\beta$-cyclodextrin was used. Despite the lower ratio values, the ascorbic acid had improved properties such as no colour change after exposure to air for one month. Storage trials were done at 38$^{o}$C and 84% humidity. The microencapsulated ascorbic acid showed slower degradation than ascorbic acid crystals.

The study concluded that:

1. Microencapsulated ascorbic acid could prevent the ascorbic acid colour change by being highly stable, it could retard the core release rate and generally mask the acid taste.

2. Using carnauba wax instead of ethyl cellulose gave a greatly reduced release ratio which is ideal.

3. Starch and $\beta$-cyclodextrin delayed the degradation of ascorbic acid when stored at 38$^{o}$C and relative humidity of 84%.

Trindade and Grosso (2000) studied the stability of ascorbic acid microencapsulated in granules of rice starch and in gum arabic. The objectives were to verify the viability of microencapsulation of ascorbic acid in rice starch and gum arabic by measuring the stability of the microencapsulated ascorbic acid, carry out a microscopic characterisation and to determine the size distribution of the microcapsules.

Using an optical microscope, they were able to observe that microcapsules were formed using both starch and gum arabic. Using polarized light it could be seen that the starch granules remained in crystalline form after the formation of agglomerates during spray drying. This indicates that gelatinisation of the starch did not occur. The starch should not undergo gelatinisation so that porous agglomerates can form. Scanning electron microscope showed the characteristic globular form of gum arabic microcapsules. Starch rice microcapsules were polyhedric, which is similar to other studies.

Microcapsules made from starch were larger than those made from gum arabic. Ninety percent of starch microcapsules had diameters ≤ 57 $\mu$m with an average of 20.5 $\mu$m while 90% of gum arabic microcapsules had diameters < 27 $\mu$m with an average of 8.0 $\mu$m.

The stability tests showed minimal losses of ascorbic acid of around 1%. Stability trials at room temperature (21$^{o}$C) and 60-65% relative humidity showed no significant losses for crystalline ascorbic acid (96.3% retained) and gum arabic microcapsules (100.7% retained). The starch microcapsules used gelatin as a binding agent at either 1 or 2% levels. The 2% level gave a more significant effect (91.6% retained) on stability than 1% level (81.3% retained). However, when the temperature was increased to 45$^{o}$C, the starch with 1% gelatin showed ascorbic acid loss of nearly 8% in the first four days of storage. When the humidity increased to 90.7%, all samples showed loss in retention for the starch, with 1% gelatin retaining the least amount of ascorbic acid with only 37% retained after 37 days of storage. The crystalline ascorbic acid remained stable with high retention over all of these conditions. The ascorbic acid encapsulated in gum arabic initially did not retain all of its ascorbic acid content, but after 23 days the retention rate remained steady at ~84% for the next 3 weeks. Thus, in terms of stability of microencapsulated ascorbic acid, this study showed that gum arabic was the best coating in spray drying.

The study used spray drying as the microencapsulation technique and highlighted that:

1. Gum arabic and starch rice microcapsules were globular and polyhedric in shape respectively.

2. Gum arabic produced microcapsules which were smaller than those made from starch.

3. Ascorbic acid coated with starch containing 1% gelatin binding agent was not very stable at room temperature, higher temperature and high relative humidity. Ascorbic acid coated with gum arabic remained relatively stable at room temperature and a change in temperature only reduced its stability slightly. Relative humidity differences did not alter the retention rate.

Dib Taxi *et al*. (2003) studied the microencapsulation of camu-camu (*Myciaria dubia)* juice. The objective of their study was to develop a process for the micro-encapsulation of camu-camu juice and optimise the operational conditions.

Camu-camu is a fruit from the Amazon that is high in vitamin C. It comes from a region where many fruits have not been studied before, so it is a natural resource with great potential. The study used spray drying as the encapsulation technique and gum arabic or malt dextrin (DE of 10) as the coating material.

The fruit was blanched at 95°C for 2 minutes and the juice extracted using a brush depulper. A mini spray dryer was used with inflow air temperatures varying between 100-160°C. Results showed that varying the wall material content and the inflow air temperature varied the yield of juice powder. When malt dextrin was used, yields were high at 12-32% wall material and temperature between 120-152°C. Outside of these parameters, yields were significantly lower. For optimum juice retention, 15% wall material and inflow air temperature of 150°C resulted in the highest juice yield of 26% and 7% vitamin C.

Microencapsulation with gum arabic showed that there was an increased yield with increase in the wall material, but temperature increase did not significantly increase the yield. Twenty percent wall material, gave maximum juice yield but vitamin C content was low at only 4%. Thus optimum conditions were 15% wall material at 150°C giving juice yield of ~24% and vitamin C yield of ~6%. The conclusion from this study was that malt dextrin and gum arabic gave the same optimum conditions to give nearly identical yield results.

Kirby *et al.* (1991) studied the stabilisation of ascorbic acid by microencapsulation in liposomes. The liposomes containing encapsulated ascorbic acid were prepared using the dehydration/rehydration method. Egg phosphatidylcholine (PC) together with cholesterol (CH) and DL-$\alpha$-tocopherol were used to form the liposomes. These were varied to study the efficiency of ascorbic acid encapsulation. Cholesterol was used to decrease liposome permeability, which was expected to increase stability. Results show no significant difference in encapsulation efficiencies with varying levels of cholesterol. All results showed around 53-58% encapsulation efficiency.

As the ascorbic acid concentration was increased, the encapsulation efficiency remained stable from 23 to 46 mM but decreased at 69 and 115 mM. Washing the encapsulant with a high osmolarity buffer brought this efficiency back up to 55%. This was done to prevent osmotic swelling and bursting which would release some of the encapsulated ascorbic acid.

During the storage trials, ascorbic acid concentration was 23 mM and storage was compared to ascorbic acid in free solution. Results showed that it took the free ascorbic acid 20 days to disappear completely from solution at 4°C and only 6 days at room temperature. By contrast, the ascorbic acid in liposomes survival times in water was greatly increased. After an initial loss in the first fifteen days, at 4°C it dropped to 60% after 50

days. At room temperature the loss was greater than that at 4°C, but still not as rapid as free ascorbic acid. After 50 days, nearly 20% of ascorbic acid was still present in the microencapsulated form. As most foods having less than 50 day shelf lives are stored in the fridge, these results at 4°C are acceptable. Products stored at room temperature that would be fortified would perhaps only have shelf lives of 10-14 days.

A potential problem with ascorbic acid is that under certain conditions it can behave as a pro-oxidant at high concentration. GC analysis of liposome phospholipid fatty acid composition after 50 days storage at 4°C revealed no evidence of substantial lipid oxidation due to encapsulated ascorbate. The fatty acid levels measured were only within 5% of the starting values.

Ascorbic acid is known to become less stable in free solution as the pH approaches neutral. The liposomes containing ascorbic acid were suspended in buffers at pH 3.5, 5.0 and 7.0. The external pH had little effect on the rate of ascorbate loss after 40 days. So it appears liposomes are able to increase the stability of ascorbic acid in differing pH solutions.

It was shown that addition of cholesterol aided ascorbic acid retention. The optimum ratio of PC:CH was 1:1 and gave ascorbic acid retention of ~60% after 40 days.

Using liposomes for microencapsulating ascorbic acid protected it from such antagonists as copper ions, the enzyme ascorbate oxidase and lysine. These were used to simulate how ascorbic acid can be lost from foods. The free ascorbate solution disappeared very rapidly in all cases but the encapsulated ascorbic acid usually maintained retention levels around 50% for all antagonists.

The study concluded that:

1. Encapsulation of vitamin C gives significant improvements to shelf life. This is true for both aqueous solutions and in the presence of common food components which would normally lead to its rapid degradation.

2. Ascorbic acid encapsulated in liposomes has applications in stabilising vitamin C in aquaculture products and vitamin protection in infant food formulations.

Watanabe *et al.* (2002) studied the effect of using saturated acyl L-ascorbate on the oxidation of linoleic acid encapsulated with maltodextrin or gum arabic by spray drying. Acyl L-ascorbate is a lipophilic derivative of L-ascorbic acid (vitamin C). It was being used in this study to examine the antioxidative ability of the ascorbates toward the encapsulated linoleic acid.

The results show that linoleic acid without ascorbate oxidises rapidly and the addition of the ascorbate slowed down this oxidation. As the molar ratios of ascorbate to linoleic acid were increased, the oxidation was reduced. The molar ratios determine the size of the oil droplets. It was shown that the higher the molar ratio, the smaller is the average diameter of the oil droplets.

So the conclusion from this study was that the addition of a saturated acyl ascorbate, especially caproyl ascorbate, to linoleic acid was effective for preparing oil droplets of small particle diameter and for suppressing the oxidation of the encapsulated linoleic acid.

Rodgers (2004) studied the use of ready meals as carriers for nutraceuticals. They fortified cook-freeze mashed potato with encapsulated vitamin C. They looked at the effect of three process treatments: a control with no vitamin C addition, ordinary vitamin C addition (33 mg/100 g) and encapsulated vitamin C addition (50 mg/100 g). Results showed that ordinary vitamin C plus potato mash was reduced slightly in fresh and freeze processes and was greatly reduced to only 2-3 mg/100 g in chill and freeze chill processes. In contrast, the encapsulated vitamin C, which started off at higher concentrations, remained high in all processes. The greatest reduction was in chill and freeze chill processes, but not

to the same degree as ordinary vitamin C plus potato mash and ~15 mg/100 g was still present. This shows that the micro-encapsulated vitamin C survived the process conditions better than ordinary vitamin C.

Desai and Park (2005) did a study of encapsulating vitamin C in tripolyphosphate cross-linked chitosan microspheres by spray drying. Its a relativley new process intended for oral delivery. Results showed a mean particle size of 6.1-9.0 $\mu$m which was influenced by the amount of cross-linking agent. Encapsulation efficiency was around 58% but decreased as the amount of tripolyphosphate solution increased. The amount of cross-linking affected the release rate and particle size.

## MICROENCAPSULATION OF OTHER VITAMINS

Vitamin C is the most common vitamin and is water-soluble. Therefore, most research make use of this vitamin. However, fat-soluble vitamin A (derived from b-carotene) is an important vitamin that merits a lot of research. It can be used to formulate foods, beverages and dietary supplements and its functions are as an antioxidant and colourant (Gerritsen and Crum, 2002). Vitamin A is found naturally in foods such as liver, fish oils, dairy products containing butterfat, and eggs. Its precursor, $\beta$-carotene, is found in plant materials such as raw carrot, mango and pumpkin, sweet potato and squash (Potter and Hotchkiss, 1995). It is essential for healthy eyes and vision, growth of bones, body's natural defence system, cell growth and reproduction (Reavley, 1998).

$\beta$-Carotene is used in dietary supplement tablets. If it leaks from a tablet and become exposed on the surface the result would be oxidation and loss of content (Gerritsen and Crum, 2002). This is where micro-encapsulation is effective.

Junyaprasert *et al.* (2001) studied the effect of various process variables on the microencapsulation of vitamin A palmitate by gelatin-acacia coacervation. The effects of colloid mixing ratio, core-to-wall ratio, hardening agent, concentration of core solution and drying method were investigated.

Gelatin-acacia microcapsules were used which entrapped microdroplets of vitamin A palmitate in corn oil. Three gelatin to acacia ratios of 2:3, 1:1 and 3:2 were used. Results showed that microcapsules were of similar sizes (~27$\mu$m), they had similar drug contents (~10-11%) and entrapped drug contents of 65-70%. The main difference was in the observations of the microcapsules. Ratios of 2:3 and 3:2 produced an aggregation of microcapsules whereas ratio of 1:1 produced expected free flowing powder. This is in agreement with the literature. The effect of core to wall ratio of 1:1 and 1:2 both resulted in free flowing powders. However, that of 1:2 resulted in a much higher entrapped drug (83% compared with 65%) and was the optimum ratio.

A hardening time of only 30 minutes did not promote encapsulation. There was no major difference between hardening times 60 and 120 minutes, so the shorter time should suit best.

Changing the core concentration did not affect the appearance or the size of the microcapsules. However, the higher the concentration, the higher was the drug content.

Different drying methods did not alter the size and shape of the microcapsules but the physical appearances were different. Air drying produced small yellow granules. Hot air drying at 40$^{o}$C produced microcapsules that were brown and sheet like. The oil usually leaked during storage. Freeze drying produced the best appearance with white powderlike granules.

Freeze-drying and air-drying both produced higher entrapped drug results than that of hot air- drying at 40$^{o}$C. However, the physical appearance of the microcapsule by freeze-drying was much better.

This study shows that process variables do affect vitamin A microcapsule properties. The optimum conditions that provided free flowing

**Table 4:** Encapsulation efficiency of vitamin C from various studies

| Study | Microencapsulation technique | Wall material | Encapsulation efficiency |
|---|---|---|---|
| Kirby *et al.* (1991) | Liposome entrapment | Egg phosphatidylcholine, cholesterol, DL-$\alpha$-tocopherol | 53-55% |
| Uddin *et al.* (2001) | Spray drying | Starch and $\beta$-cyclodextrin | ~50% |
| Dib Taxi *et al.* (2003) | Spray drying of camu-camu juice | Malt dextrin | 26% juice yield with 7% vitamin C yield |
| Desai and Park (2005) | Spray drying | Tripolyphosphate cross-linked chitosan | 55% |

**Table 5**: Particle size of microcapsules of vitamin C from various studies

| Study | Microencapsulation technique | Wall material | Average microcapsule diameter ($\mu$m) | % between particular fraction |
|---|---|---|---|---|
| Uddin *et al.* (2001) | Spray drying | Gel, starch, ethyl cellulose and $\beta$-cyclodextrin | | 60-70% between 90-280 $\mu$m |
| | | Carnauba wax | 50 $\mu$m | |
| Trindate and Grosso (2000) | Spray drying | Rice starch | 20.5 $\mu$m | 90% <57 $\mu$m |
| | | gum arabic | 8.0 $\mu$m | 90% < 27$\mu$m |
| Watanabe *et al.* (2002) | Spray drying of linoleic acid | Maltodextrin | Median ~1.0 $\mu$m | |
| | | Gum arabic | Median ~ 0.2 $\mu$m | |
| Desai and Park (2005) | Spray drying | Tripolyphosphate ross-linked chitosan | 6.1 to 9.0 $\mu$m | |

powder with a high percentage of entrapped drug were 1:1 gelatin:acacia ratio, 1:2 core:wall ratio, 60 minutes of hardening time and 40% w/w vitamin A palmitate in corn oil as the core material.

Vitamin C and vitamin E can be used synergistically as an antioxidant. Vitamin E acts as the primary antioxidant, reacting with and repairing free radicals, and it is itself then regenerated itself by the vitamin C. Liposome entrapment can be used to protect these vitamins (Kirby *et al.*, 1991).

## CONCLUSION

The stability of vitamins, especially vitamin C, is greatly improved by microencapsulation.

Different techniques of encapsulation produce the same results. Processes can be optimised by choosing the optimal wall material, core to wall ratios, additives and temperatures to give the most stable product possible with the most material encapsulated.

Microencapsulated vitamins are used for nutritional purposes to fortify foods and as antioxidants. The increased stability in foods makes them ideal for use in breads, infant formulas, cereal bars and dairy products.

## REFERENCES

Apintanapong, M., and Noomhorn, A. 2003. The use of spray drying to microencapsulate 2-acetyl-1-pyrroline, a major flavour component of aromatic rice. International Journal of Food Science and Technology, 38: 95-102.

Desai, K. G. H. and Park, H. J. 2005. Encapsulation of vitamin C in tripolyphosphate cross-linked chitosan microspheres by spray drying. Journal of Microencapsulation, 22 (2):179.

Dib Taxi, C. M. A., Menezes, H. C. D. E., Santos, A. B. and Grosso, C. R. F. 2003. Study of the microencapsulation of camu-camu (*Myciaria dubia)* juice. Journal of Microencapsulation, 20 (4): 443-448.

Dziezak, J. D. 1988. Microencapsulation and encapsulated ingredients. Food Technology, 4:136-159.

Gerritsen, J. and Crum, F. 2002. Getting the best from beta-carotene. International Food Ingredients, 3: 40-41.

Gibbs, B. F., Kermash, S., Alli, I. and Mulligan, C. N. 1999. Encapsulation in the food industry: a review. International Journal of Food Sciences and Nutrition, 50: 213-224.

Herald Sun. 2005. Medicinal munchies. In Burstin Fay (Ed). Herald Sun Newspaper, p. 26, May 27.

Higgins, S., Carroll, Y. L., O'Brien, N. M. and Morrissey, P. A. 1999. Use of micro-encapsulated fish oil as a means of increasing n-3 polyunsaturated fatty acid intake. Journal of Human Nutrition & Dietetics, 12 (4): 265-272.

Junyaprasert, V. B., Mitrevej, A., Sinchaipanid, N., Broome, P. and Wurster, D. E. 2001. Effect of process variables on the microencapsulation of vitamin A palmitate by gelatin-acacia coacervation. Drug Development and Industrial Pharmacy, 27 (6): 561-566.

Kirby, C. J., Whittle, C. J., Rigby, N., Coxon, D. T. and Law, B. A. 1991. Stabilisation of ascorbic acid by microencapsulation in liposomes. International Journal of Food Science and Technology, 26 (5): 437-449.

Korhonen, H. 2002. Technology options for new nutritional concepts. International Journal of Dairy Technology, 55 (2): 79-88.

Potter, N. N. and Hotchkiss, J. H. 1995. Food science. 5th edn. New York: Kluwer Academic / Plenum Publishers.

Reavley, N. 1998. Vitamin counter. The vitamin content of common foods. Australia: Bookman Press.

Risch, S. J. and Reineccius, G. A. (Eds). 1995. Encapsulation and controlled release of food ingredients. USA: American Chemical Society.

Rodgers, S. 2004. Value adding with functional meals. Food Service Technology, 4: 149-158.

Rosinski, S., Grigorescu, G., Lewinska, D., Ritzen, L. G., Viernstein, H., Teunou, E., Poncelet, D., Zhang, Z., Fan, X., Serpy, D., Marisony, I. and Hunkeler, D. 2002. Characterization of microcapsules: recommended methods based on round-robin testing. Journal of Microencapsulation, 19 (5): 641-659.

Schrooyen, P. M. M., van der Meer, R. and Kruif, C. G. 2001. Microencapsulation: its application in nutrition. Proceedings of the Nutrition Society, 60: 475-479.

Shah, N. P. and Ravula, R. R. 2000. Microencapsulation of probiotic bacteria and their survival in frozen fermented dairy desserts. The Australian Journal of Dairy Technology, 55 (3): 139-144.

Shahidi, F. and Han, X. Q. 1993. Encapsulation of food ingredients. Critical Reviews in Food Science and Nutrition, 33 (6): 501-547.

Trindade, M. A. and Grosso, C. R. F. 2000. The stability of ascorbic acid microencapsulated in granules of rice starch and in gum Arabic. Journal of Microencapsulation, 17 (2): 169-176.

Uddin, M. S., Hawlader, M. N. A. and Zhu, H. J. 2001. Microencapsulation of ascorbic acid: effect of process variables on product characteristics. Journal of Microencapsulation, 18 (2): 199-209.

Vilstrup, P. 2001. Microencapsulation of food ingredients. England: Leatherhead Publishing.

Watanabe, Y., Fang, X., Minemoto, Y., Adachi, S. and Matsuno, R. 2002. Suppresive effect of saturated acyl L-ascorbate on the oxidation of linoleic acid encapsulated with maltodextrin or gum Arabic by spray drying. Journal of Agriculture and Food Chemistry, 50: 3984-3987.