Effect of wall structure and formulation on O_2 barrier of spray dried flavorings

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INTRODUCTION

Flavour compounds by nature are volatile, reactive and may be unstable to heat, light or oxygen. Thus encapsulation is commonly used to protect flavourings and facilitate their delivery in a food application. Of the processes available for flavour encapsulation, spray drying is used to produce in excess of 90% of these dry flavourings (Porizo, 2012). While there are numerous performance criteria for these encapsulates, the ability to protect from oxygen is one of the most important for any flavouring containing oxidizable components (most notably citrus essential oils). Since many flavourings do contain some citrus oils, the oxygen barrier properties of the encapsulant wall material has received substantial attention over time.

Historically gum acacia was the wall material of choice for flavour encapsulation. Over time modified starches (hydrolysed and reacted with octenyl succinic acid anhydride (OSAn)), have become common alternatives to gum acacia. These two materials offer some oxygen barrier properties for the flavouring but this attribute is variable with gum acacia source and typically very poor for the modified starches. Early research showed that including some low molecular weight components, e.g. sugars or high DE corn syrup solids, substantially improves the oxygen barrier properties of the wall matrix (Anandaraman et al., 1986). This has an added benefit of reducing costs since these materials are typically much lower in cost than either the modified starches or gum acacias.

Research has also shown that using proteins for flavour encapsulation (entirely or a part of the wall matrix) also is effective in providing an effective oxygen barrier (Moreau et al, 1996). Unfortunately while effective, the use of proteins as a wall material offers numerous disadvantages such as being (relatively) expensive, reactive towards any carbonyl components in the flavouring, may be unstable in final applications (ppt in acid solutions) and requires that the flavouring be labelled a potential allergen (Charve et al., 2009)). Thus, we seldom proteins used in flavour encapsulation other than for coacervated flavourings. Unfortunately, complex coacervation requires an amphoteric food polymer and proteins generally serve this purpose (chitosan is the only other candidate for this role).

In a recent study on the effect of wall material type on flavour stability to oxidation, we noted that not only wall formulation determined oxygen barrier properties, but also the spray drier infeed solids levels (Charve *et al* 2009). This observation prompted some additional research which will be presented and discussed, as well as some prevailing theories on how wall material influences the barrier properties of a spray dried particle.

MATERIALS AND METHODS

The encapsulation (spray drying) of a mixture of limonene, citral, (E)-2-hexenal and cinnamaldehyde was done using two different wall materials (modified starch and gum acacia (*seyal*)) at two different solid levels (gum acacia at 30 and 10% infeed wall solids; modified starch at 40 and 10%). The wall material was initially dispersed in warm water (40C) at the desired solids level and kept under constant stirring overnight to ensure hydration. Just prior to spray drying, citral, (E)-2-hexenal and cinnamaldehyde (5% each, v/v) were blended with limonene (85%, v/v) and added to the carrier slurry at a 1:4 ratio flavour:carrier solids and homogenized with a high shear mixer (Greerco Corp., Hudson, NH) at high speed for 5 min. The conditions during spray drying were inlet and exit air temperatures of 200 ±5C and 100 ±5, respectively. The four samples were prepared in duplicate. After cooling to room temperature, the powders were stored in a desiccator (35C) under controlled water activity (saturated $MgCl_2$ solution, a_w=0.33 at 25C) for 40 days.

Samples were taken periodically and analyzed for the retention of flavouring materials and the formation of oxidation products (i.e. limonene oxide) by gas chromatography.

RESULTS AND DISCUSSION

Beginning with some discussion about how wall material functions to provide an oxygen barrier, numerous theories exist. A "picture" commonly presented is that spray dried particles may have cracks and fissures in them that allow oxygen pathways into the particle mass (Figure 1). Over time more comprehensive and detailed explanations have evolved. The work of Townrow et al. (2007) has served as the foundation for current thinking, i.e.

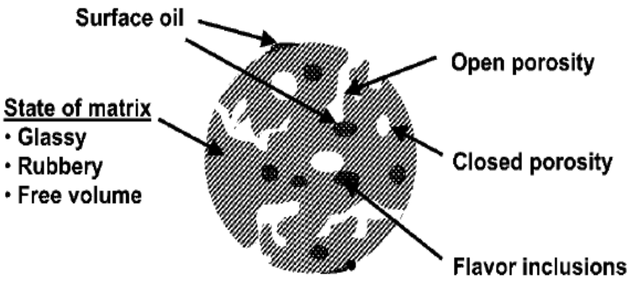

Figure 1. Structural defects in glassy encapsulation matrices. (Ubbink et al, 2003)

molecular packing is the factor that controls wall material permeability to oxygen. A unified theory has been established that links the properties of a wall material formulation and environmental conditions (e.g. temperature and water activity) to oxidative protection (Ubbink, 2012).

The work we discuss today does not deal with formulation or environment but processing conditions (i.e. specifically spray dryer infeed solids concentration). In the past, most flavour companies have predicted oxygen barrier properties based on the molecular weight distribution of a wall composition. However, the data presented in Figure 2 illustrates how oxygen barrier properties of a given wall material can differ based on infeed solids.

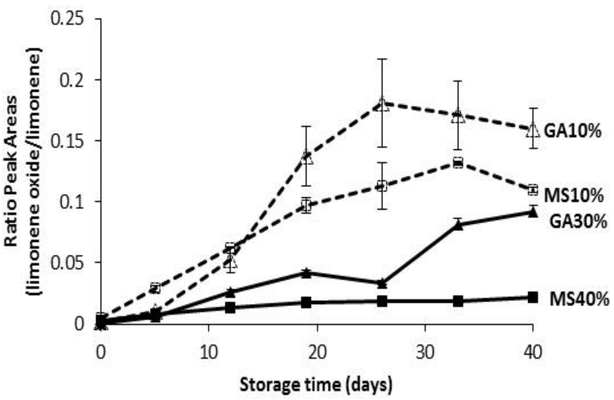

Figure 2. The influence of infeed solids during spray drying on the oxidation of limonene during storage (MS is modified starch; GA is gum acacia; the % shown is the infeed carrier concentration during spray drying).

It is relevant that the oxygen barrier properties of both carrier materials were strongly dependent on infeed solids. This supports the data originally presented by Charve et al. (2009) showing a similar effect across selected carbohydrate and protein wall materials. The explanation for this observation is that infeed solids influences particle density and thus molecular packing: higher infeed solids means greater molecular packing thereby serving to inhibit the diffusion of molecular oxygen into, or through the dry particle. A bottom line conclusion is that manufacturers should be not only considering wall formulation but also processing conditions when producing dry flavourings that contain oxidizable flavouring components.

It is interesting that dryer air temperatures have not shown a similar effect for one might expect dryer operating temperatures to also have an effect on molecular packing. Very commonly the use of high dryer infeed air temperatures result in particles of lower density i.e. molecular packing.

REFERENCES

- Anandaraman, S. *et al.* (1986). *Stability of encapsulated orange peel oil*. Food Technol. 40(11):88-93
- Charve, J *et al.* (2009). *Encapsulation Performance of Proteins and Traditional Materials for Spray Dried Flavors.* J Agric Food Chem. 57(6), 2486-2492
- Moreau, DL *et al,* (1996) *Oxidative stability of anhydrous milkfat microencapsulated in whey proteins*. J Food Science 61(1): 39-43
- Porizo, M. (2012). *Advances in flavor encapsulation*. Food Technology. 52-64
- Townrow, S. *et al.* (2007) *Molecular packing in amorphous carbohydrate matrixes*. J. Phys. Chem. 111, 12643-12648
- Ubbink, J., *et al.*. (2003) *Flavor delivery systems*. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, J. Wiley & Sons, 527-563.
- Ubbink, J. (2012) M*aterials science approaches towards food design*. In: *Food Materials Science and Engineering* B. Bhandari & Y. Roos, Eds. Wiley-Blackwell Publ., Chichester, UK pp 107-203.