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THE MICROSTRUCTURE OF SPRAY-DRIED MICROCAPSULES

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Abstract

A newly developed technique for SEM sample preparation has been applied in the study of the effects of process parameters on the microstructure of gum arabic spray-dried microcapsules. The technique, that employs embedding in an apolar resin and partial polymerization, makes it possible to simultaneously observe the inner and outer structure of microcapsules. Our results show how the core material is organized in the solid wall matrix, existence of one or more internal voids in the microcapsule, indentation and caps in the exterior of the microcapsules, and how these microstructural features are affected by solids concentration in the sprayed emulsion, and by feed and drying air temperature.

Introduction

Microencapsulation is a packaging technology by which liquid droplets or solid particles are packed into continuous individual shells. The shells (or 'walls') are designed to protect the encapsulated material ('coating') from the factors that may cause its deterioration. In different applications, microcapsules are designed for controlled release of the core material under desired conditions, and at predetermined rate. Microencapsulation techniques in general, and in the food industry in particular, have been extensively reviewed, e.g. Bakan (1973), Balassa (1971), Graves (1972), Herbig (1970), McKernan (1972, 1973) and Puisieux and Benita (1984). In the food industry, the technique has been mainly used for the encapsulation of volatiles and oxygen-sensitive materials, using mostly spray-drying techniques (Todd, 1970, Graves, 1972, and Kirby and Law, 1987).

Successful microencapsulation is the result of a judicious choice of wall material composition for a given core material. The protection afforded by the wall and the flow properties of the encapsulated product depend on the inner and outer microstructure of the capsule, and on how the core material is organized within the microcapsule. These factors are readily studied by scanning electron microscopy (SEM) in the secondary electron imaging (SEI) mode, with great depth of field and sufficiently high resolution (Rosenberg et al., 1985). In this paper we describe the application of improved SEM techniques to study the effects of wall composition and drying conditions on the inner and outer structure of spray-dried microcapsules.

Materials and Methods

Microcapsules were prepared by
Rosenberg et al.

Spray-drying emulsions of the core material in aqueous solutions of the wall material. As model core material we used ethylbutyrate, ethylcaproate, and ethylcaprylate (analytic grade from Frutarom, Israel). These were chosen to represent a wide range of solubilities in conjunction with retention and shelf life studies to be published separately by these authors. The wall material in all the experiments described here was gum arabic (technical grade from Sharon Laboratories, Israel). Emulsification was carried out using an XL020 microturrax homogenizer (Interlabs App. GmbH), and spray-drying in a mobile Minor Niro-atomizer spray dryer. Feed rate to the spray dryer was 15 g/min, and feed temperature was usually 20 °C (except for specific experiments described below). Experiments were performed at inlet air temperatures of 100, 150, and 250°C that give rise to outlet air temperatures of 70, 90 and 140°C, respectively. Atomizer speed was usually 30,000 rpm. Emulsion drop sizes were determined by light microscopy; emulsion viscosities were measured by a Brookfield viscometer at 25°C.

SEM specimen preparation procedures have been described in detail in previous publications (Rosenberg et al., 1984, 1985). To study their outer structure, microcapsules were attached to an SEM stub by a two-sided adhesive tape, and gold-coated (15 nm layer) in a Polaron E515 sputter-coater. To study the inner structure of the capsules, the powder was embedded in the apolar resin, Lowicryl HM-20 (Polaron, U.K.), and sectioned in an 820 rotary microtome (American Optical). A modification to the previously described embedding method is presented in the results section. The sectioned blocks were then mounted on SEM stubs, and gold coated. Specimens were examined in JEOL T-200 and T-300 SEMs in the secondary electron mode.

Figure 1: Gum arabic spray-dried microcapsules containing 20% caprylate on a dry basis (DB) with increasing solids concentration (w/w): (a) 10%; (b) 20%; (c) 30%; (d) 40%. Drying conditions: air inlet/outlet temperatures 150 °C/90 °C, emulsion feed temperature 20 °C.
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imaging mode, at acceleration voltage of 25 kV. Microcapsule average size was determined from points on SEM micrographs at magnifications of about 2000X. At least 100 particles were counted for each population.

Results

The effect of solids concentration in the continuous phase of the spray-dried emulsion is shown in Figures 1a, 1b, 1c, 1d from experiments in which the drying conditions were fixed: inlet air temperature of 150 °C, outlet air temperature 90 °C, and feed temperature of 20 °C. The core material (ethylcaprylate) content in these experiments was 20% on dry gum arabic basis ("20%DB"). Different magnifications were used in the various parts of the figure to show large microcapsule populations, or to emphasize detail.

At solids concentration of 10, 20 and 30% the produced microcapsules exhibited the same outer geometry of spherical particles with fairly deep indentations. These indentations were not present at the highest concentration checked of 40%. In all cases no cracks or pores could be seen in the microcapsule wall. The mean size of the particles increased with solids concentration: 10.5, 11.0 and 20.5 μm for 10, 20 and 30% solids, respectively. A wide particle size distribution was found in all experiments. This is attributed to the atomizer properties. At 40% solids, the microcapsules were much larger; many of them were not spherical, but rather elongated. This is probably linked to the viscosity of the continuous phase that increased sharply with solids concentration: 10, 23, 84 and 250 centipoise for the four concentrations examined. Solids concentrations might also affect the amount of shrinkage of the drying emulsion droplets.

Figure 2 illustrates the effect of feed and air temperature on the outer structure of the formed microcapsules. Figures 2a and 2b show the effect of raising feed temperature. The reduced temperature difference between feed and drying-air causes less shrinkage of the capsule. Another phenomenon, possibly due to slower cooling, but higher inside temperature, is the formation of caps inside some of the indentations (Figure 2b). A similar phenomenon is observed when the drying air is very hot, e.g., 250 °C, as seen in Figure 2c. In this case, heating of the gas or vapor trapped within a capsule is very rapid and the outward growth of the cap is as fast as, or faster than, the shrinkage due to water loss. The result is sometimes almost smooth spheres, or in some cases exploded ones (Figure 2d). At a lower drying air temperature, shrinkage is the dominant factor as can be seen in Figures 2a and 2e. The lower solid concentration of the microcapsules of Figure 2e caused more pronounced shrinkage than in Figure 2a. At a still lower drying-air temperature of 100 °C (Figure 2f), microcapsules with only shallow indentations were produced. This is a result of a lower rate of drying which causes uniform shrinkage of gum arabic in the walls. Microcapsule size is also affected by rate of drying. Many large capsules with diameters up to 40 μm are found in batches dried at 250 °C or at high feed temperature (75 °C), whereas at feed temperature of 40 °C and drying air temperature of 150 °C the mean diameter is only 10 μm. This value rises to 15 μm when the feed temperature is raised to 50 °C. This finding is also related to the increasing expansion of microcapsules at the above-mentioned conditions.

To study the inner structure of the microcapsules, they must be opened. The most efficient way to do this is to embed the microcapsule powder in a resin, polymerize it, and fracture the resulting block, so that the fracture surface includes open microcapsules. In previous publications (Rosenberg et al., 1984, 1985), we demonstrated the feasibility of embedding in Lowicryl HM-20, an apolar resin that does not damage the embedded capsules, and that is polymerized by UV radiation at room temperature or even much below it. But with this technique it is impossible to determine where the cutting plane passes through a capsule. This makes it ambiguous whether a capsule has a large or a small central void, and where that void is located within the capsule. To overcome these problems we modified our preparation technique. We found that a reduced polymerization time (20 minutes instead of 40 minutes at 10°C, using the manufacturer's recommended resin-to-crosslinker ratio, two 15W UV (360 nm) lamps at a bulb-to-sample distance of 35 cm) the center of the resin block is only partially polymerized. If the block is fractured through this region, the residual unpolymerized microcapsules-in-resin suspension can be removed using a needle, leaving behind a hole in the block. At the edges of this hole one can find many fractured capsules that are only partially embedded in the resin matrix. By tilting the microcapsule tray, one can then observe simultaneously the inner and the outer structure of such a capsule, and thus determine where the capsule has been fractured. An example is given in Figures 3a, 3b, 3c, 3d which show a hole in the resin matrix and its edges at increasing magnifications.
Figure 2: The effect of liquid feed and drying-air temperatures on spray-dried microcapsules. (a) 20% (w/w) gum arabic in emulsion (GA=20%); 20% ethylcaproate on dry basis (EC=20%), feed temperature, FT=20°C; air inlet and outlet temperatures, AT=150°C/90°C; (b) same as (a) but FT=75°C; (c) same as (a) but AT=250°C; (d) same as (c) but GA=30%; (e) GA=10%, EC=20%, FT=20°C, AT=150°C/90°C; (f) same as (e) but AT=100°C/70°C.
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Figures 3c, 3d show the inner and outer structure of a microcapsule that was fractured through its center. One can clearly see the position of the typical large central cavity, the limited effect on its shape by the outside 'dimples', and the distribution of the core material within the shell.

This new sample preparation method was used to determine the effect drying-air temperature has on the inner structure of the microcapsules. Figures 4a and 4b show microcapsules dried at 100°C. In most microcapsules no central voids were found. This was checked by examining many particles at the edges of holes in polymerized blocks, making sure that the cutting plane did not miss possible voids by passing above or below them. In all cases where microcapsules did have voids, these were small and located in the center of the capsule. The core material was found to be dispersed in the wall in small droplets, 0.5-1.5 µm in diameter. These droplets were well isolated from the outer surface of the microcapsules. No channels or cracks connected them to the outer surface. The deep indentations or 'dimples' that had been observed before from the outside can be clearly seen here in cross-section.

When the drying-air temperature was increased to 150°C, central voids were found in many more microcapsules (e.g., Figure 4c). In some cases, more than one void, up to four interconnected voids, were found (Figure 4d). The wall thickness of microcapsules with central voids varied from 5 to 10 µm depending on the size, shape, and location of the void within the microcapsule, and

Figure 3: Fractured SEM specimen, of spray-dried gum arabic microcapsules containing 20% ethylbutyrate prepared by embedding in Lowicryl HM-20 resin and incomplete polymerization: (a) a low magnification image of the hole in the resin block; (b) a higher magnification micrograph showing the edge of the hole; (c) a higher magnification of (b) showing simultaneously the inner and outer structure of microcapsules; (d) magnified detail of (c); note the distribution of core material in the wall and the structure of the central void.
Figure 4: The effect of drying conditions and solids concentration on the inner structure of gum arabic spray-dried microcapsules: (a) GA=30%, ethylcaprylate concentration ECY=30%, FT=20°C, AT=100°C/70°C; (b) GA=20%, ECY=20%, FT=20°C, AT=100°C/70°C; (c) GA=20%, ECY=20%, FT=20°C, AT=150°C/90°C; (d) GA=20%, no core material, FT=20°C, AT=150°C/90°C; (e) GA=10%, EC=10%, FT=20°C, AT=250°C/140°C; (f) GA=20%, EC=20%, FT=20°C, AT=250°C/140°C.
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whether deep indentations in the outer surface of the microcapsule were present. In some cases these indentations distorted the central void geometry. Drying with 250°C air produced smooth, indentation-free balloon-like microcapsules with very large central voids (Figures 4e and 4f). In the other cases, void occupied most of the microcapsule volume; the wall thickness in these cases was only 2-5 μm.

Discussion

The microstructure of spray-dried systems determines the product bulk density, porosity, and volatile core material retention. Despite the importance of microstructural information, very little of it has been available so far. Several theoretical and semi-empirical models describing the behavior of carbohydrate systems during spray-drying have been developed nevertheless, e.g., Menting et al., (1970), Kerkhof (1975) and Schoeber (1976), who assumed spherical drops with no internal voids, that shrink uniformly during drying. Van der Lijn (1976) suggested a mechanism for a drop expanding during spray-drying because of an expanding air bubble trapped in it. A similar mechanism of expansion was suggested by Verhey (1972a, 1972b, 1973). Air may be trapped in the liquid during atomization, before drying. Charlesworth and Marshall (1960) attributed expansion of particles during spray-drying to the formation of steam bubbles within the liquid drops. In a more recent work, Greenwald (1980) claimed that the internal void within spray-dried particles is a result of air desorption from the liquid fed into the spray-dryer.

Our results, that provide direct inner and outer microstructural data on the microcapsules, indicate that the frequency of finding voids and their average size increase with increasing drying temperature under the same atomization conditions. The almost total absence of voids in microcapsules dried at 100°C suggests that air bubble incorporation during atomization is negligible, and that the voids are the result of either air desorption or steam generation, or both. Higher drying temperatures cause these bubbles to expand considerably and offset, partially or totally, the shrinkage of the wall material due to loss of water. The overall result in the extreme cases are very thin walls, and occasionally exploded microcapsules.

The deep indentations or 'dimples' in the exterior of the microcapsules were found to occasionally also affect the structure of the inner voids. These indentations are probably the result of water loss from the drying drop, and are formed during the early stages of the process (Greenwald, 1980). This hypothesis is supported by our finding that at intermediate drying temperatures, "caps" develop within these dents, and that at high temperatures, the indentations disappear altogether. The expansion, therefore, must take place after dent formation, but when the wall material still contains enough water to be elastic and malleable. Conditions which favor slow drying rates were also found to favor the formation of smoother particles, since in that case, loss of wall and shrinkage were more uniform. High solids concentrations give rise to viscous drops. These were found, as expected, to be larger than those formed from less viscous emulsions. Shrinkage in this case is slower than at low solids concentration because of smaller surface area-to-volume ratio, and because of higher viscosity. The drops also shrink less in this case because of less water to be lost from the system during spray-drying.

Under all the conditions studied, we found that the core material is dispersed as small droplets, 0.5-20 μm in diameter, in the solidified continuous wall material. This size range is identical to the size range of core material drops found in the emulsion fed into the spray-dryer. The micrographs of fractured microcapsules also showed that core material droplets are protected well by the matrix, and that no losses are expected as long as the wall remains intact. It was found that at a given solids concentration and drying conditions, the increasing core material concentration led to thinner wall layers around each core drop.

The question of retention of the volatile core material during microencapsulation, i.e., how much of the emulsified material actually becomes microencapsulated, has not been addressed in the present paper; it will be discussed in a separate publication (Rosenberg et al., in preparation). Suffice here to say that our SEM work has revealed that substantial core material losses may occur during the initial stages of drying. This is demonstrated by Figure 5 in which there is no evidence of any ethylbutyrate remaining from an initial concentration of 10%. The loss must have occurred before complete solidification, since all the drops (or 'pools'), where the ester had been embedded in the matrix, disappeared.

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The emulsion contained originally 10% (DB) ethylbutyrate which was lost during spray-drying, as evident from lack of small "pools" in the fractured microcapsules.

Acknowledgment

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AT</td>
<td>air temperature: (inlet temperature)/(outlet temperature)</td>
</tr>
<tr>
<td>DB</td>
<td>concentration on a dry basis</td>
</tr>
<tr>
<td>EC</td>
<td>concentration of ethylcaproate on a dry basis</td>
</tr>
<tr>
<td>ECY</td>
<td>concentration of ethylcaprylate on a dry basis</td>
</tr>
<tr>
<td>FT</td>
<td>feed temperature</td>
</tr>
<tr>
<td>GA</td>
<td>concentration of gum arabic in emulsion</td>
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References


Discussion with Reviewers

Reviewer II: Figures 2a and 2b are interesting. I am very surprised that higher infeed temperature produces larger particles. Is this supported in the literature?
Authors: The phenomenon was not observed. The magnification of Figure 2b is almost twice that of Figure 2a; also, in Figure 2b we show two large particles to emphasize detail.

Reviewer II: The difference in appearance of Figures 4a and 4b is not clear. The same for 4c and 4e and 4f. One part of the figure looks like clearly distinguished particles, and the other an embedded particle. Why are there such differences?
Authors: The differences stem from the variation of the embedding technique used: whereas Figure 4a is an example of fully embedded particles (in a fully polymerized resin block), Figure 4f is an example of partially embedded particles (close to the hole in the partially polymerized resin block; see text and Figure 3 for details), allowing views of both inside and outside of the microcapsules.

Reviewer III: Do the authors feel this method could be applied to other dried systems, like milk or corn sweeteners?
Authors: The method can be used with any dried system. The embedding resin should be selected according to the properties of the system.

Reviewer IV: What are the implications of using such high temperatures for the materials that are to be encapsulated? This would be especially of importance for volatile compounds.
Authors: The quantitative aspects of volatiles retention during microencapsulation, including temperature effects are discussed in detail in a paper by these authors, to be submitted for publication soon.