Melt Extrusion and Melt Injection

An in-depth look at the strengths, limitations and applications of these two processes

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The flavorist has a number of options with which to encapsulate a liquid flavor. These commercially viable systems have been noted[1] and are re-listed in **T-1**. Each encapsulation system brings with it a number of constraints, and the choice of the best-suited process is critical to a successful delivery of the encapsulated flavor.[2] Melt extrusion and melt injection are two similar process systems. Unfortunately, some juxtaposition of these terms has occurred in the literature, which can lead to confusion. This article discusses the strengths, limitations and various applications of these two flavor encapsulation processes.

Nomenclature

Terms referring to extrusion encapsulation have been used interchangeably for similar but distinct processes. These terminologies include: extrusion, extrusion encapsulation, melt-extrusion, hot-melt extrusion, polymer-melt extrusion, glass encapsulation, melt encapsulation, melt-injection and Durarome process. The major distinction lies in the use of either a twin-screw extruder (melt extrusion and extrusion encapsulation) or the hard candy syrup-boil process followed by injection and cooling of the syrup flavor into a solvent bath (melt injection and Durarome process). A profile comparison of the two systems is found in **T-2**.

Early Commercial Systems: Melt Encapsulation

L. Sair and R. Sair were early inventors utilizing a pre-extrusion melt technology to encapsulate flavors, food ingredients and vitamins.[3] They described the use of a plow-mixer (Littleford mixer) to blend flavors, oils or nutrients into the carrier in a closed system. Their process employed food polymers hydrated under mechanical shearing to form a plastic mass. A flavor was then mixed into the plastic mass and forced into smaller shapes. However, the use of increased levels of water (20–50% based upon carrier + flavor), which acted as a plasticizer to generate the rubbery exudate mass, also required a finishing drying step to obtain a stabilized amorphous solid. L. Sair also modified the process by lowering water levels, using a single screw extruder and generating a dense glassy solid by having the hot melt flow into a restricting take-off tube.[4]

Melt Extrusion (Extrusion Encapsulation)

The melt extrusion or melt encapsulation process utilizes a twin screw co-rotating extruder to melt a carbohydrate polymer carrier under pressure into a viscoelastic fluid state. A liquid flavor (compounded, extract, reaction, oleoresin, etc.) can be added to the feed stream at the inlet port of the extruder. Alternatively, the same liquid flavor can be injected under pressure into the molten mass within the extruder where it is mixed before exiting the die head. Carbohydrate polymers are usually employed

Commercial encapsulation systems **T-1**

Encapsulation system	Relative contribution (%)[a]	Preferred physical state
Spray drying	~80–85	Glassy solid—fine powder
Lipid: spray chilling	5–10	β-Polymorph—fine particles
Melt extrusion	2–3	Glassy solid—particulates
Lipid: flakes	1	β-Polymorph—flakes
Melt injection	2	Glassy solid—threads
β-Cyclodextrin molecular complex	1	Crystalline complex
Complex coacervation	< 1	Cross-linked polymer membrane surrounding flavor droplet
Co-crystallization	< 1	Crystalline sucrose with occluded flavor

[a] personal communication – F. Paulicka

Extrusion encapsulation **T-2**

System	Melt injection	Melt extrusion
Flavors	O/S, W/S	O/S, W/S, reaction
Claimed flavor loads	10–20%	7.5–40%
Practical flavor loads	10–12%	8–12%
Carriers	sugars, maltodextrins, corn syrup solids	sugars, maltodextrins, corn syrup solids, food polymers modified starches, salts, acids, acid salts
Volatiles	yes	yes
Process	batch	continuous
Commercial scaling	difficult	simple
Production efficiency	low	high
Solvents required	yes	no
Chilling baths	yes	no
Air cooling	no	yes
Final state	glassy threads	glassy matrix (threads, ropes, sheets)
Technology status	in public domain	carriers patented

with sugars. Low levels of water are employed as a plasticizer to obtain an efficient "melting" of the matrix utilizing the mechanical and thermal energies of the extruder. The use of co-rotating screws allows for positive conveyance and pressure control of the plastic rubbery mass as it mixes and passes forward through the die. US Patent 5,807,461 uses a twin-screw extruder to melt a modified starch/maltodextrin/corn syrup solids/mono- or disaccharide mixture containing a spray-dried flavor.[5] A more practical enhancement of melt extrusion technology was disclosed in the patents assigned to McCormick and Co., Inc.[6] In this system the matrix composition was selected to generate a plastic flavor-matrix exudate that upon cooling rapidly transformed into the glassy state. With simple process adjustments the encapsulated flavor-matrix can be continuously generated, cooled to the glassy state, milled, sieved and packaged in a continuous process to generate FlavorCell products (See **F-1**). Extruders, being robust mechanical systems, can be run continuously 24/7 while encapsulating flavors. This leads to the obvious advantage of low cost production for large volumes of encapsulated flavor products.

While the FlavorCell extrusion system operating parameters remain proprietary, this system depends upon a careful balancing of those operating parameters including matrix formula, flavor (levels, co-solvents, emulsifiers), melt temperatures, screw and die design, operating pressures and exit temperatures. By selecting die geometries, extrudates can be produced as fine threads, rods, ropes or sheets. Examples of some of these materials have been previously described.[7]

Protective and controlled-release functionalities can be built into the flavor carrier. Some preferred polymers that can generate these functionalities include gelatins, pectin(s), alginates, proteins and exudate gums.[8] However, the increased molecular weights and melt viscosities of some polymers over normal carbohydrates reach the limits of some processing parameters.

Porzio and Zasypkin detailed the physical characteristics of melt-extruded compositions employing modified starch (OSAN starches)-sugar blends.[9] They evaluated physical properties such as viscoelastic character (i.e., elastic recovery) as well as extruder operating parameters and final product state in terms of the glassy state character (i.e., the glass transition temperature [Tg] and degree of glassy character [ΔCp] of the encapsulated flavors). In this study the identical carriers and flavors were also spray dried and the two encapsulated systems compared for selected physical properties.

As noted, this encapsulation technology is covered in part by a number of patents that disclose specific flavor-matrix compositions. These matrices supply the flavorists with carefully matched carriers for specific flavors. For example, a fruit flavor might utilize a maltodextrin/organic acid/acid salt matrix blend for desired acidity, sensory characteristics and flavor impact.[10]

Very functional polymers for melt extrusion are the gelatins and hydrolyzed gelatins.[11] In specific cases flavor loads up to 15–20% (w/w) flavor were noted. Also the levels of surface oils were extremely low, exhibiting < 0.001% by weight of surface oil, based on the total weight of the composition. However, gelatin will also react with flavor aldehydes and ketones to generate imine intermediates and derivatives and potentially unbalance the flavor sensory character.

In recent USPTO-published applications, the use of specific polymers to form a flavor exudate yielded a claimed hydrogel.[12,13] In this case high flavor loads of up to 40% by weight were posited with the expectation that immersion of the flavor-matrix would generate a swollen (rubbery) state and control release of the flavor.

Melt Extrusion and Pressure Cooling

A modification of the melt-extrusion system specifically addressed the issue of volatile flavor loss and flavor top note retention. Ordinarily extruder melt temperatures operate at 105–125°C, which can lead to "flashing" or vaporization of moisture, low boiling flavors and solvents as the melt exits the die into ambient pressure. Fulger and Popplewell overcame this problem by cooling the molten exudate-flavor mass under super-ambient pressures (20–30 atmospheres) as it cooled and formed the glassy state.[14–16] The result upon scanning electron microscopy (SEM) characterization was a dense glassy solid with no evidence of pores from escaping volatiles. When encapsulating acetaldehyde and diacetyl, the pressure-cooled product showed increased particle densities and enhanced flavor retention. However, no information was supplied in these patents regarding extended retention and stability, but one should expect a densified matrix to have superior retention properties of volatiles over the ambient pressure equivalent.

One proposed modification of a twin screw melt-extrusion encapsulation system could include use of a chilling solvent bath to both set (cool) and rinse the extruded fibers, threads or ropes. However, this modification would come with added steps and costs of the solvent handling and finish drying.

Commercial Product Lines

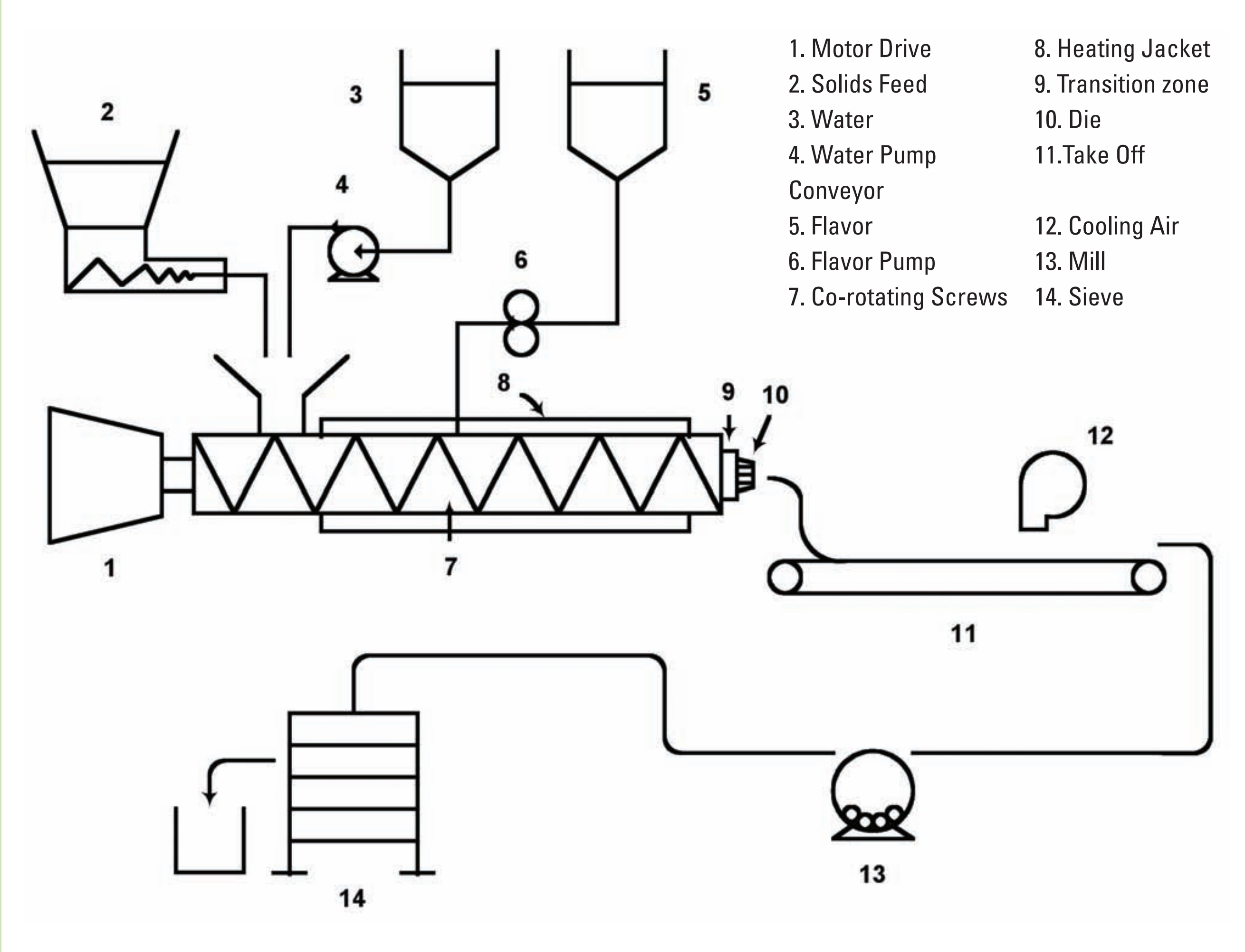
A number of similar encapsulated flavor product lines using variations of the melt extrusion and melt injection process and carriers are now commercially available. These include melt extrusion systems such as FlavorCell (McCormick and Co., Inc.), CapLock (IFF) and Evoglass (Symrise); and melt injection systems such as Durarome and Flexarome (both Firmenich).

Melt Injection (Durarome Process)

The second major extrusion encapsulation procedure—preferably designated as melt-injection encapsulation—is based upon the confectionary hard candy procedure of boiling down sugar syrups.[17–20] In these systems a sugar, mixed sugars or sugar/corn syrup solids solution is prepared and excess water boiled off. At the very high syrup solids levels temperatures can reach in excess of 300°F (149°C) for continuous moisture removal. In a variation of this encapsulation process, the sugar syrup must be placed in a jacketed pressure kettle, excess water boiled off under either vacuum conditions or at ambient pressure, flavor (and color) added, the pressure lid sealed and the stirrer used to disperse the added flavor oil. Following emulsi-

Melt extrusion process (courtesy of Ken Hsu of McCormick and Co., Inc.)

F-1



fication of added flavor by high shear mixing, the closed system is pressurized and the sugar-flavor fluid injected through narrow orifices into a cold solvent bath at ambient pressure. Usually the solvent of choice is isopropanol. The threads of the extruded mass rapidly solidify, generating an amorphous solid with flavor droplets dispersed within the carbohydrate mass. Additional processing steps are necessary to drain and remove the bulk solvent, followed by hot air removal of any residual solvent from the solid. This melt-injection process is often referred to as the Durarome process, named after the trade name of the first commercial product line of encapsulated flavors.

The greatest advantage of this system involves the immediate solvent cooling and concomitant removal of any terpene-based surface oil. Citrus oils are notoriously susceptible to limonene oxidation, generating limonine epoxide that becomes objectionable as an off-flavor in the ppm range. Products such as instant drink mixes and flavored teas have become key users of the Durarome melt-injection encapsulated citrus flavors.

The original process, as reported by Swisher, employed a corn solids syrup cooked down to 3–8% moisture, to which a citrus oil was added to form an emulsion, and this emulsion was cooled off to obtain a solid encapsulated matrix.[17] The same inventor later modified his process by taking the hot carbohydrate-oil emulsion described in the original process and injecting the molten mass through narrow orifices into a chilled isopropanol bath.[19]

The use of the chilling solvent to remove surface oils played a significant role in making the melt-injection process a preferred process in protection against surface flavor oxidation. However, when one considers the dimension of the thread diameter (1–5 mm) in relation to the flavor droplet diameter (20–100 microns), there is a large probability of interior oil being freshly exposed as the thread is cracked or broken.

Beck describes a similar process but utilizes sucrose with corn syrup solids to encapsulate essential oils at approximately 10% flavor load in the carbohydrate matrix.[21] The hydrolyzed corn solids are needed to prevent crystallization of the sucrose that is in an amorphous state in the solid matrix.

Another approach using melt-injection was taken by Firmenich with its polymer system that utilized 1–7% agar-agar in the matrix.[22] Subsequent hydration of the solid flavor-matrix yielded a gelled matrix with claimed controlled-release functionality.

Melt Injection—Static Pressure Cool: Pop Rocks

One unique variation of the basic hard candy melt-injection encapsulation process cools the high solids syrup with gas under pressure in a closed static system. This batch process produced a unique flavored candy—Pop Rocks. In this process, the sugar syrup was first vacuum-boiled to remove the bulk water. The hot concentrated syrup was then moved into a manifold pressure chamber and flavors (and colors) were introduced. The syrup was equilibrated with gaseous CO_2 by stirring the molten mass under pressure in the makeup chamber. Next, the pressurized low moisture amorphous sugar mass was directed into cooling tubes and cooled statically in place under pressure. After solidification, the tubes were depressurized, the bulk solidified sugar released and then processed (in a low humidity environment) into specific particle size ranges. This colored, flavored, glassy sugar matrix was marketed as the novelty candy Pop Rocks or Cosmic Candy. The sugar particles would release the pressurized CO_2 upon being placed in the mouth and hydrated. The sensation from the rapid release of gas and built-in stress in the carbohydrate matrix was literally a popping sensation in the mouth. A short book by Rudolph details the rise and demise of this candy at General Foods.[23] He also describes some interesting events in solving manufacturing problems encountered scaling up from a laboratory Parr reactor to commercial production.

This novel sugar matrix indicates that a low molecular weight volatile gas such as CO_2 can be successfully encapsulated, stabilized and retained under the proper environment for extended periods of time. This author retained a consumer sample of an identical licensed product made by Zeta Espacial in its original packaging in a closed container for five years. Evaluation of the stored product by sensory response indicated the sugar retained CO_2 and exhibited the "popping" sensation. Modulating Differential Scanning Microscopy [MDSC] profiles from the original sample and the five-year stored sample revealed that the key transitions [Tg and ΔCp] were identical. This retention of properties suggests that the self-diffusion of a low molecular weight volatile can be significantly limited under the proper conditions in a unique glassy matrix.

Summary: Extrusion Encapsulation

The basic processes of melting a carrier solid, mixing in flavor and solidifying the encapsulated flavor-matrix are similar but distinct for the methods described above. From a manufacturing and cost basis, melt extrusion using a twin-screw co-rotating extruder will always be the most efficient production system. The melt injection or Durarome process has the advantage of being in the public domain with all relevant patents expired. It is a batch versus continuous process that requires the use of solvents. In each system oil-soluble flavors are easily encapsulated. Water-soluble flavors can be limiting in both systems where water, ETOH or propylene glycol co-solvents can affect the properties of the matrix as plasticizers.

One additional benefit from melt extrusion can be the ability to extrude food hydrocolloids and polymers for added control-release functionality. Very little has been reported on this aspect of physical chemistry of extruded polymer mixtures as flavor control-release agents in the trade literature. However, the increasing use of melt extrusion with selected food polymers should yield more functional controlled-release products for both water-soluble and oil-soluble flavor systems.

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