Functionalized Flavors

Formulation and challenges

Mike Porzio, Flavor Delivery Systems

Flavorists working with the food industry, and to a lesser extent the personal care and nutraceutical fields, should be aware of a trend that is quietly, but increasingly, impacting their business—the commoditization of flavors.

This business dynamic is due to a confluence of trends: unrelenting pressure for price reductions by industrial clients with the strategy of supplying flavor samples to alternate flavor houses for "matching" briefs. These briefs are supported by access to sophisticated analytical systems, such as time of flight mass spectrometers (TOF/MS), to analyze those flavors. These instruments give analytic chemists the capability to identify all key flavor components and this information can be supplied to the flavorists working on the matching brief. Here the flavorists' intent is not necessarily the duplication of an exact flavor formula, but the development of an *organoleptically equivalent* flavor with reduced costs. Once this cost reduction process starts, the cycle ends when profit margins are squeezed to an absolute minimum. One approach to protecting flavors is technical insulation by using unique and proprietary delivery vehicles for the flavors.

The Alternate Strategy

By marrying a flavor to a functional carrier, the resulting flavor system is insulated from duplication and becomes a functional and value-added product. Currently there are a number of nascent encapsulation and delivery systems that need to be evaluated in this effort. Some of these approaches are described here.

Nanoemulsions

There are two distinct routes to preparing nanoemulsions, both of which involve nanoparticles (flavor droplets) dispersed in a continuous medium. Here the nanoparticles are characterized as oil droplets with a size range of 50–500 Angstroms (0.05 to 0.50 microns).

One of the nanoemulsion systems has already been used by the flavor industry in the form of solubilized flavor oils. However, the term *nanoemulsion* was not used to describe these solubilized oils when they were first developed. The term "microemulsion" was later used to describe these unique phases in the technical literature.[1]

In this system, the oil droplets form a thermodynamically stable phase by spontaneous generation of sub-micellar droplets using surfactants and alcohols as co-solubilizers. These oil droplets are stabilized into a size range that does not reflect incident light. Therefore, the system appears to be a clear or colored solution. A large number of composition patents for microemulsion systems comprising water/flavor oil/surfactant(s)/alcohols can be found in the US Patent and Trademark Office patent files.

An alternate route to nanoparticle dispersions or nanoemulsions requires extreme mechanical dispersion of the oil phase. In fact, current homogenizing equipment used in generating normal flavor emulsions already produces a small population of sub-micron sized particles. By increasing the energy of shear forces on the flavor oil phase, the sub-micron-sized particle population can be maximized. Proper attention to the choice of specific processing equipment is key to produce nanoemulsion preparations. In addition to specific process equipment, there are formulary requirements for agents to stabilize the oil droplet interface. These stabilizing agents are proteins or peptides as well as surfactants. Unlike the nanoemulsions (microemulsions) these nanoparticle dispersions are not thermodynamically stable and will behave as normal flavor emulsions.

OrganoGels

Flavors are generally found in two states: liquid flavors and dry flavors (spray dried, melt extruded or melt injected glassy states). A third option is formation of flavor gels. These gels are a result of the interaction of the liquid flavor components with specific polymers. Here the flavor can act as a solvent—solvating the polymer to form a gelled phase. These materials are sometimes referred to as organogels or lipogels.[2] Fruit and dairy flavors with their low molecular weight esters, aldehydes, acids, ketones and alcohols are ideally suited to function as solvents to solvate the selected food polymer(s). Hydrophobic flavor systems such as the terpene-based citrus flavors or other flavor oils interact weakly, if at all, with the food polymers and are more difficult to obtain as organogels.

When the interaction of the solvent (flavor) with the selected polymer is weak and not sufficient to completely solvate the polymer, additional solvation energy in the form of heat can shift the flavor-solvent polymer energy balance and produce the flavor gel upon cooling.

An alternate option is to add a solvent that interacts strongly with the gel-forming polymer to the liquid flavor. In some cases the co-solvent will interact very strongly to form a solvent-polymer gel, but exclude the flavor as a separate liquid phase. In a more preferred case the flavor plus co-solvent will function as a single phase and form the homogeneous organogel. These determinations are easily performed in the laboratory using a sealed test tube to mix the flavor (and co-solvent) with a polymer and allowing the system to equilibrate under ambient conditions overnight.

Once a flavor organogel has been formed, volatile components of the flavor can slowly diffuse from the gel over time. However the added functionality and control release properties of such a system make this gelled state a functionalized flavor.

Lipid Sub-α States

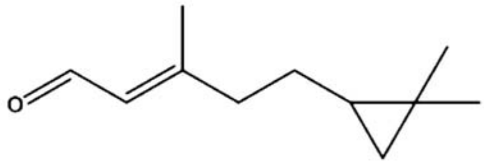
There are a number of lipid encapsulation techniques being practiced that constitute a significant percentage of the current encapsulation options.[3] Some lipid encapsulation systems employ hard fats to form a thin lipid film on particles and a moisture protection barrier with thermal release properties. A significant contribution of lipid-encapsulated flavors comes from "spray chilling." This process generates flavors entrained in fine solid lipid particles. A study of the physical chemistry of the hard fat transitions shows that fats slowly transform or recrystallize into progressively more stable polymorphic forms: α, β-prime and β. As the recrystallization process proceeds through the stages $\alpha \rightarrow \beta' \rightarrow \beta$, the liquid flavor phase is slowly expelled from the crystalline lattice and the initial encapsulation characteristics are slowly degraded.

For a skilled lipid chemist there is another method to consider—that of preparing the lipid in the non-crystalline sub-α state (α_{sub}). The sub-α form will be a metastable amorphous triglyceride solid. By stabilizing this triglyceride sub-α state at room temperature, a "lipid-glass" can be generated. There are two possible routes to generate this unusual solid. The first approach would be to identify and purify triglycerides with selected fatty acid profiles that would self-inhibit polymorphic state formation. The alternate approach would be addition of *polymorphic inhibitor(s)* to the molten triglyceride fat to prevent crystallization of the solid fat into polymorphs. This approach would improve the current fat encapsulation technologies significantly without requiring any changes in current processes.

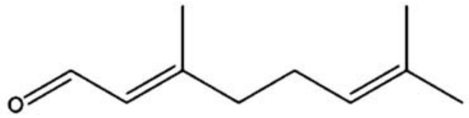
Rationally Designed Flavors

A refined theory of smell, as postulated by Turin, is based upon the (vibrational) bond strength of the molecule and is now becoming more accepted after its initial rejection by the perfumery industry.[4] This theory is verified by commercial practice in terms of "rationally designed flavors."[5] An excellent example is the design and preparation of a citral analogue. This compound, commercially known as Acitral* [FEMA# 4105; (E)-5-(2,2-dimethylcyclopropyl)-3-methylpent-2-enal], was designed to be an acid stable citral analogue with a lemonlike flavor character.

Acitral, FEMA# 4105, (E)-5-(2,2-dimethylcyclopropyl)-3-methylpent-2-enal; Citral, FEMA# 2303, 3,7-dimethyl-2,6-octadienal **F-1**



ACITRAL - FEMA# 4105
(E)-5-(2,2-dimethylcyclopropyl)-3-methylpent-2-enal



CITRAL - FEMA# 2303
3,7-Dimethyl-2,6-Octadienal

Substitution of the terminal double bond of the citral molecule utilizes a cyclopropane moiety. The cyclopropane ring is made up of a pair of sp^2 orbitals in the form of "banana bonds." This bond hybridization of cyclopropane is similar to the sp^2- sp^2 double bond in citral with its overlapping p orbitals, but lacks the reactivity to protonation by acids. However, the bond characteristics are similar in strength, mimicking the same vibrational characteristics, which are the basis for the organoleptic character. Acid-initiated degradations found with citral are retarded by several orders of magnitude in the presence of acids with the Acitral.

SuperGlasses

In a recent article on melt extrusion and melt injection an observation was recorded that a PopRocks product—a confectionery carbohydrate carrier pressurized with CO_2 and cooled under pressure into the glassy state—exhibited an unexpected stability response.[6] After being stored in a dry environment at ambient conditions for five years, an analysis of the sample showed identical MDSC profiles and retention of significant levels of entrapped CO_2 when compared to the original material. This finding suggests that the normal self-diffusion characteristics of small volatile molecules in a glassy matrix can be significantly retarded. Using that assumption, addition of specific "packing" molecules that reduce the molecular free-volume paths within the bulk glass environment should lead to increased retention of flavor volatiles. Also non-pressurized encapsulation systems, such as spray drying, may be used to generate a glassy matrix containing stabilized volatile flavor compounds such as dimethyl sulfide, ethanol, acetic acid, acetaldehyde and diacetyl.

---

* Acitral is a trade name of Flexitral; *www.flexitral.com*

Thermal Stable Flavors

One specific request developers and flavorists often receive is for thermal stable flavors, i.e. flavors that can withstand the extreme thermal processing environments found in baking, extrusion, canning and frying. Under these harsh process conditions the flavors will degrade, volatilize or become unbalanced. A number of flavor encapsulating systems have been evaluated and can supply limited protection. Some of these approaches include lipid encapsulation using very high melting lipids or waxes, complex coacervation and multiple layered coatings of flavored particles. Each of these has practical and technical limitations. Future routes to thermal stabilization need to be evaluated by studying food polymer-flavor interactions for specific and irreversible high temperature phase responses.

Flavor Modulation

The most exciting new route for the functionalization of flavors is based upon newer discoveries in the understanding of "flavor modulation systems." This biochemistry is in its earliest stages of development and is based upon discoveries of neurophysiology and cellular biochemical signaling pathways involved with flavor and taste perception by receptor sites.

By understanding the role of multiple sub-cellular signal pathways and feedback loops that constitute signal transduction, it should be possible to enhance flavors and tastes or mask undesirable organoleptic signals in a controlled manner. A reasonable strategy can identify known signal modifiers and use them to make up specific carriers for a flavor. If the flavor is married to this carrier a new version of a functionalized flavor could be obtained.

For example, with cheese the complex interaction of flavors and tastes result from the organoleptic and gustatory responses to the salt, proteins, aromatic acids and dairy flavors constituting the cheese product. To prepare a cheese flavor modulating carrier, a characteristic cheese flavor would first be compounded; then the modulating carrier made up of a number of specific enhancing agents would be tested at various use levels. Milk proteins, salts and acids would be added to the carrier system to balance and complement the enhancing agents. A flavor emulsion could then be prepared and spray dried. The resulting modulated flavor should be able to replace, in part, real cheese solids in a seasoning.

Flavorist and Functionalized Flavors

A flavorist should recognize that a great deal of physical chemistry needs to be applied to obtain the above-mentioned flavor functionalization. These technical objectives can be efficiently executed only if flavorists work in close cooperation with a resident encapsulation specialist, each bringing in the necessary skills to identify and generate these unique and proprietary flavor systems.

References

1. L Prince, *Microemulsions in Theory and Practice*, Academic Press, London (1977)
2. JH Van Esch and BL Feringa, New Functional Materials Based on Self-Assembling Organogels: From Serendipity towards Design, *Angew Chem Int Ed*, 39(13), 2263–2266 (2000)
3. S Gouin, Microencapsulation: Industrial Appraisal of Existing Technologies and Trends, *Trends in Food Science and Technology*, 15, 330–347 (2004)
4. L Turin, A Spectroscopic Mechanism for Primary Olfactory Reception, *Chemical Senses*, 21, 773–791 (1996)
5. L Turin, *The Secret of Scent*, HarperCollins, New York (2004) 185–186
6. M Porzio, Melt Extrusion and Melt Injection, *Perfum Flavor*, 32(6) 48–53 (2008)

Address correspondence to Mike Porzio, Flavor Delivery Systems, PO Box 382, Hunt Valley , MD 21030, mporzio9@comcast.net.

To purchase a copy of this article or others, visit www.PerfumerFlavorist.com/magazine. p&f