Scalping of Flavors in Packaged Foods
M.G. Sajilata, K. Savitha, R.S. Singhal, and V.R. Kanetkar

ABSTRACT: Food packaging, although an integral part of the food chain, has a major drawback in that, often, the packaging material interacts with the flavor constituents of the food, causing either a selective or an extensive loss of desirable food flavors or absorption of undesirable off-flavors from the packaging material, thereby resulting in an eventual loss of quality of the packaged food item. The process is called “scalping” and is of great concern to the food industry, which is always looking out for new avenues in “packaging solutions” for its final product quality needs. The review highlights the various attributes of the scalping process, explores approaches to the reduction of the manifested undesirable effects, and covers other relevant aspects.

Introduction

Food packaging in recent years has experienced rapid advances and continuous growth due to consumer desire and demand for conveniently packaged products. This has promoted a trend in packaging materials that has evolved from simple food wraps to sophisticated containers. Besides providing an adequate shelf life and product quality, it is desirable that the packaging material also participates in the overall flavor management of the packaged food, flavor being an underlying factor in the consumer acceptability of all food products. However, sorption of food aromas, particularly by plastic packaging materials, is usually perceived as a major factor contributing to the quality alteration of most foods during storage. This causes changes in both the intensity and characteristics of the food flavors owing to their absorption by the packaging material, a phenomenon commonly referred to as “scalping” (Roland and Hotchkiss 1991).

Flavor scalping is a term used in the packaging industry to describe the loss of quality of a packaged item due to either its volatile flavors being absorbed by the package or the food absorbing undesirable flavors from the packaging material. The inability to prevent scalping is a sore point for many packagers, a classic example being the absorption of various plastic flavors when soft drinks are stored in plastic bottles for an extended period of time. Tropicana discovered that its gable-topped orange juice cartons scalped flavor from the juice by absorbing important chemicals. Polyethylene (PE), the most common plastic used in commercial products, including beverages, is a top scaler.

Commercial plastics for food packaging include simple homopolymers or copolymers such as low-density polyethylene (LDPE), medium-density polyethylene (MDPE), high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), aluminum sheet (Surlyn), ethylene vinyl alcohol copolymer (EVOH), and others (Gremli 1996). Figure 1 shows the molecular structures of the polymers used as packaging materials (Willige 2002). Among the plastic materials, polyethylenes and polypropylenes (homo- and copolymers) are mostly used in package design preferred for contact with the product both in monolayer and laminated or coextruded structures because of their good chemical resistance and inertness to most foods, good barrier properties to water, and thermosealability. However, their polyolefinic nature gives them high lipophilicity enabling retention of large amounts of nonpolar compounds such as most of the aroma compounds, thereby causing an aroma imbalance in the packaged food. Trace concentrations of residual solvents, monomers, plasticizers, inhibitors, or mold-release agents conceivably could migrate to the food product and, also, flavor ingredients can travel to the package. Moreover, flavor scalping from the product does not require the product to be in direct contact with the polymer because the aroma compounds are volatile enough to transfer from the headspace to the package. Thus, although the polymeric films may be adequate moisture or gas barriers for a product, these benefits can be offset by flavor scalping. Studies in scalping will therefore help determine the type of plastic films best suited for a particular food product (Risch 1991). The frequent use of PE on the inner surface of the food-contact polymer containers has made it the principal polymer in most scalping studies.

Interaction between Food Flavor and Packaging Material

The first and foremost function of a food package is to protect the product and preserve its inherent quality (Nielsen and Jägerstad 1994). Over the past decade, the use of plastic packages has increasingly replaced metal and glass for food and beverage packaging, the advantages being numerous—lower costs, lighter in weight, less apt to shatter, transparent, flexible, and convenient to the consumer. In spite of all these advantages,
there are some properties of plastics that limit their use in food packaging (Salame 1989). Food packaging interactions, defined as an interplay between food, packaging, and the environment, can produce an adverse effect on the food and/or the package (Hotchkiss 1997). Interactions between the plastic package and the flavor constituents can cause adsorption and absorption of flavor volatiles by the packaging material, permeation of the flavor volatiles through the plastic material, and food- and flavor-induced changes in the physical properties of the plastic polymer, as well as interactions of low-molecular-weight compounds in the plastic such as solvent and plastifiers with the food flavor or the food itself, thereby resulting in an overall imbalance in the flavor profile of the food (Gremli 1996).

Figure 2 shows the possible interactions between foodstuff, polymer film, and the environment and their adverse consequences (Nielsen and Jagerstad 1994). Flavor losses that result from interaction with the polymer package can be either losses occurring by permeation or migration through the package or those from sorption by the container (Strandburg and others 1991).

Modeling Studies in Flavor Scalping

There are several models, more aptly theoretical considerations, to predict the losses due to flavor scalping. Flavor losses that result from interaction with the polymer package can be either losses occurring by permeation or migration through the package or those from sorption by the container (Strandburg and others 1991).

The permeation process can be described as a multistep event. First, collision of the penetrant molecule with the polymer is followed by sorption into the polymer. Next, migration through the polymer matrix occurs and, finally, desorption of the permeant from the polymer completes the process. For a polymer with thin film geometry, Fick’s first law can be written as

$$\frac{\Delta M_x}{\Delta t L} = \frac{P A \Delta p_x}{\Delta L}$$

where $\frac{\Delta M_x}{\Delta t L}$ is the transport rate of the material $x$ through a film of area $A$, with a thickness of $L$, and under a chemical potential created by pressure difference across the film of $\Delta p_x$. $P$ is the permeability coefficient and is a steady-state parameter.

$$P = DS$$

The permeability consists of 2 parameters, the diffusion coefficient $(D)$ and the solubility coefficient $(S)$. The diffusion coefficient is a kinetic parameter. It is a measure of how fast transport events will occur. It reflects the ease with which a penetrant molecule moves within a polymer host. The diffusion coefficient is determined from the following equation:

$$D = \frac{L^2}{7.2 t_{1/2}}$$

where $L$ is the film thickness and $t_{1/2}$ is the time required to reach one-half the steady-state mass transport rate. Once the permeability coefficient and the diffusion coefficient have been obtained, the solubility coefficient can be calculated.

The solubility coefficient is a thermodynamic parameter. It is a measure of the concentration of penetrant molecules that will be in position to migrate through the polymer.

$$C_x = S p_x$$

where $C_x$ is the concentration in the polymer and $p_x$ is the partial pressure of $x$ in the vapor phase.

The sorption of the flavor ingredient from solution onto the polymer involves the process of partitioning and diffusion. The mechanism of sorption consists of both adsorption onto the solid surface followed by dissolution into the polymer and diffusion away from the surface under the driving force of a concentration gradient until equilibrium is established. The partitioning step involves adsorption onto the polymer surface and mixing into the polymer matrix, which depends on the relative forces of attraction between the solution and the polymer for the solute. These forces are governed by the thermodynamics of the system and are affected by structure and polarity. These factors can be considered on the basis of cohesive energy density (CED) forces or its square root, the solubility parameter of the Hildebrand equation.
The Hildebrand approximation for the heat of mixing is

$$\Delta H_m = v_1 (\delta_1 - \delta_2) H_f^2$$

where $\Delta H_m$ is the partial molar heat of mixing, $v_1$ is the partial molar volume of the penetrant, $\Phi_1$ is the volume fraction of the polymer in the mixture, and $\delta_1$ and $\delta_2$ are the square roots of the CED of the penetrant and the polymer. The differences in the CED values of the polymer-penetrant combination in a given system will affect the size of heat of mixing and a permeant with a larger CED will have larger heat of mixing and less negative $\Delta G$ than the one with a smaller CED.

The diffusion step depends on the mobility of the solute, which can depend on its size and interaction with the polymer to plasticize and relax its chain segments (Halek and Luttmann 1991).

Organic vapors often solvate host polymers that eventually exhibit increased permeability to oxygen and other gases suggesting that oxygen permeability might provide information on volatile diffusivity of the penetrant and the polymer oxygen permeability at time $t$, and $M_0$ and $P_a$ are the corresponding volatile weight and polymer oxygen permeability at $t = \alpha$. If results are expressed as a dimensionless ratio, then oxygen permeability can be used to solve mass transfer equations. Crank (1967) presented an applicable equation for membrane absorption and desorption (Sadler and Braddock 1990, 1991). As oxygen permeability is directly proportional to penetrant concentration, $M_t/M_0$ will be equal $P_t/P_a$, where $M_t$ and $P_t$ are, respectively, the absorbed volatile weight and oxygen permeability of the polymer at time $t$, and $M_0$ and $P_a$ are the corresponding volatile weight and polymer oxygen permeability at $t = \alpha$. If results are expressed as a dimensionless ratio, then oxygen permeability can be used to solve mass transfer equations. Crank (1967) presented an applicable equation for membrane absorption and desorption (Sadler and Braddock 1990, 1991), where

$$\frac{M_t}{M_0} = \sum \frac{18 \exp[-D(2n+1)^2\pi^2t)]/(2n+1)^2\pi^2]}{4\pi^2}$$

and the absorption equation is $\frac{M_t}{M_0} = 1 - \frac{M_t}{M_0}\text{desorption} = 1 - \frac{M_t}{M_0}\text{absorption}$, where $D$ is the diffusion coefficient, and $\tau$ is the membrane thickness when both surfaces are exposed to the penetrant. For single-surface penetrant exposure, $\tau$ is the full thickness of the membrane.

Migration testing using food simulants is the normal procedure for checking compliance of a food packaging material against specific migration limits (SMLs). However, as Feigenbaum and others (2002) point out, this is not practical for several reasons. Industries that put packaged foods or materials intended for food contact on the market do not know the identity of the potential migrants; sometimes, those who manufacture and sell these raw materials do not know the processing conditions or the final application; and even if the identity of the migrants were known it may be difficult to analyze them. Therefore, the use of mathematical modeling to predict migration, which can reduce the amount of tests to be undertaken, has been recently introduced into legislation. Practical examples for the application of this new concept are described in the Practical Guide (European Commission 2003).

Mass transfer from a plastic into food consists essentially of kinetic (diffusion in the polymer and foodstuff) and thermodynamic (equilibrium partitioning between the packaging and food) factors, besides the geometric dimensions of a given food/packaging system. The most important variables that control migration of the substances are contact time $t$ and temperature $T$. Numerous migration tests have shown that the majority of measurements could be represented as being approximately proportional to the square root of $t$ and the initial concentration of the migrant in the polymer, $c_{P,0}$. With the assumption that material transport obeys the law of diffusion, the following equation can be applied to describe approximately the migration of a substance from a polymer into a food (simulant) for situations where $m_{t, \infty} < 0.5$:

$$m_{t, \infty} = 2k_{P,d}(D/\pi t)^{1/2}$$

where $D_P$ is the actual diffusion coefficient of the migrant in the polymer with a homogeneous distribution of the migrant at an initial concentration, $c_{P,0}$. The constant $k$ is the measure of the influence of factors that lie outside the polymer/migrant system and has, by definition, a value of $k = 1$ in the absence of such influences (such as for contact with ethanol and oil) as long as no polymer swelling takes place. A practical application of this equation is that for cases with $k = 1$, the actual diffusion coefficients of migrants in the polymer can be determined from the kinetic measurement of $m_{t, \infty}$ from systems with known/measured values for $c_{F,0}$. Provided that the migration potential in the polymer, that is, the initial amount of migrant dissolved in the polymer, $m_{P,0}$, is known, then

$$m_{t, \infty} = \frac{m_{P,0}}{1 + k_{P,F}(V_P/V_f)}$$

The partition coefficient $k_{P,F}$ is defined as the concentration ratio at equilibrium of a migrant in the polymer, $c_{P,F}$, divided by that at equilibrium in the foodstuff or food stimulant, $c_{F,0}$. The values for $k_{P,F}$ range over several orders of magnitude, depending on the polarity of the polymer involved, the food stimulant, and the nature of the migrant. The $k_{P,F}$ value for limonene, a nonpolar substance in the LDPE/water system at 23 °C, was found to be higher than 5000. This makes it retained in the polymer, whereas a much more polar compound such as cis-hexenol shows a much lower value of 0.33, causing considerable transfer into water.

In recent years, the possibility of modeling with easily available hardware and software opens a large field of complex applications. MIGRATEST Lite (1997, 1999), COATING TEST (1999), and MIGRATEST (2000) are specialized softwares offered for migration modeling (Brandsch and others 2000).

Sorption of Food Flavors by the Packaging Materials

Sorption of food flavors in polymers involves the process of both partitioning and diffusion. Moreover, although the intensity of aroma of a packaged foodstuff depends on the vapor pressure (influenced by the other food components), interaction of the volatile organic moieties with other food constituents, and aroma barrier characteristics of the package (Mahoney and others 1988), the nature of the aroma is also imperative in determining the extent of sorption. The extent of flavor absorption is influenced by the properties of the polymer, the flavor molecules, and also external conditions. The chemical composition, chain stiffness, morphology, polarity, and crystallinity of the polymer influence flavor absorption as much as the chemical composition, concentration, and polarity of the flavor compounds, as well as the presence of other chemical constituents. External factors such as duration of storage, relative humidity, temperature, and the presence of other food components can also affect the solubility of aroma compounds in a polymer (Nielsen and others 1992a; Leufven and Hermansson 1994).

Some of the major factors influencing the scalping process are described in detail below.
Flavor Characteristics

Concentration

The higher the concentration of the sorbed material, the higher the rate of transport into the polymer structure (Brody 2002). The presence of coperoxidants can affect the rate of transport of the molecules through the polymer usually by increasing the rate.

Carbon chain length, boiling point, and polarity

The carbon chain length is closely related to the boiling point of a molecule, and several researchers have indicated a relationship between solubility and boiling points of sorbates. Thus the carbon chain length of volatiles affects their solubility in polymer films. In a sorption study, permeation and diffusion of volatile compounds into PE or ethylene vinyl copolymer films were evaluated using volatile compounds such as alkanes, aliphatic ethyl ethers, aldehydes, and alcohols containing 4 to 10 carbon atoms. Sorption and solubility coefficient were found to increase with an increase in the carbon chain length of the volatile compounds. A study on the sorption behavior of flavor compounds by PE liner of laminated pouches (PET/Al/PE) containing 43 volatile compounds showed the distribution ratio of the flavor compounds to increase with carbon chain length of the flavor compounds from 0.01 to 0.1 for alcohols, 0.03 to 1.23 for aldehydes, 0.02 to 5.77 for aliphatic esters, and 0.11 to 11.6 for benzoates (Shimoda and others 1988). The distribution ratio, defined as the ratio of amount sorbed into PE film and the adhesive layer to the amount remaining in the solution with respect to each flavor component, was used as the basis of comparison. In each series, the distribution ratios increased about 3-fold for each methylene group, but in the compounds composed of 11 or more carbon atoms, the increments were either less or, in the case of aldehydes, negative. The sorption of esters, ketones, and aldehydes by PP has also been shown to increase as the number of carbon atoms in the compounds increased. Moreover, compounds with 8 or more carbon atoms were demonstrated to be sorbed from yogurt drinks by HDPE with shorter molecules remaining in the product (Linssen and others 1991). In the same study, it was observed that highly branched molecules were sorbed to a greater extent than linear molecules.

Esters and aldehydes are reportedly absorbed much more than the alcohols in LDPE. The absorption of aldehydes has been correlated to their structure, the shorter chain aldehyde, decanal, being absorbed to a lesser extent than the C12 aldehyde, and dodecanal. The chain length of the lipophilic portion of the molecule appears to affect its absorption, the unsaturated aldehydes (for example, perillaldehyde and geranial) being absorbed to a lesser extent than the saturated aldehydes (Charara and others 1992). The length of the carbon chain might account for the differences between the esters; the longer the chain, the lesser the polarity and ease of absorption of the compounds by the nonpolar polyolefins.

According to Shimoda and others (1988), the effect of functional groups on the distribution ratios of flavor compounds between a film and a solution was greater in the liquid phase because of closer interactions, whereas the effect of molecular weight or boiling point was much larger than the functional group in the vapor phase. Strandburg and others (1991) obtained a linear relationship between the logarithm of the solubility coefficient in vinylidene chloride copolymer and the boiling point of linear esters, alkanes, and ketones. Similar results are reported for the solubility of alkyl esters in polyvinyl alcohol (Landois and Hotchkiss 1988). The higher solubility of linalool compared to limonene in PE is also shown to be influenced by its boiling point. Linalool is a more linear, less bulky molecule than limonene, which would facilitate its ability to move into the polymer matrix. In addition, its higher boiling point (198 °C for linalool, 175 °C for limonene) is indicative of its ability to condense and remain within the matrix (Roland and Hotchkiss 1991). Boiling point has been correlated to higher solubility by several workers. Also, linalool, usually present at 1/10 the concentration of limonene, may have a greater potential in affecting aroma due to sorption by a PE package than limonene. The higher solubility of linalool coupled with its higher sensory impact increases the effect of linalool sorption. Figure 3 and 4 differentiates linalool and limonene with respect to their structures.

Solute polarity is one of the predominant controlling factors influencing sorption. Flavors are absorbed more easily in a polymeric film of similar polarity. The sorption of a number of citrus flavors by LDPE is almost instantaneous, the partitioning depending on the polarity of the compounds. Comparing car- vone (C10H18O) and limonene (C10H16), both similar terpenes but with different polarity, it has been shown that the less polar limonene is not only sorbed at a faster rate but also diffuses more rapidly, probably due to lesser cohesive forces (Halek and Luttman 1991). In the sorption of citrus oil constituents by polyolefins, terpenes showed the highest affinity for the polymers, followed by sesquiterpenes (C15); larger amounts of esters and aldehydes were sorbed than alcohols, due to polarity (Charara and others 1992). For the same reasons, saturated aldehydes were sorbed to a greater extent than those with double bonds.

Orange juice aromas have been demonstrated to be sorbed to different extents, starting with hydrocarbon compounds, which showed the highest affinity to LDPE, followed by ketones, esters, aldehydes, and finally alcohols (Linssen and others 1991; Nielsen and others 1992a; Linssen and Roozen 1994). Factors that affect absorption include molecular size of the aroma compounds and polarity and solubility properties of both the polymer and the aroma compounds. Table 1 shows the solubility parameters and hydrogen-bonding characters of aroma compounds and the polymers used in the study by Nielsen and others (1992b). In general, the smaller the difference between δ values of the polymer and the flavor compound, the greater the solubility of the flavor into the polymer. Alcohols have much larger solubility parameter values than LDPE, LLDPE, and PP, which might explain why they

Figure 3 – Structure of linalool

Figure 4 – Structure of limonene
are less absorbed compared to esters and aldehydes while PET has a solubility parameter closer to that of the alcohols. Also, polarity and hydrogen-bonding character play an important role in the prediction of solubility. The reason why the alcohols are not absorbed to a greater extent into PET might be due to their strong hydrogen-bonding character, which PET lacks. Esters and aldehydes have solubility parameters very close to LDPE, LLDPE, and PP, which partly explains their large partition coefficient in these polymers. The differences between the esters might be accounted for by the length of the carbon chain—the longer the chain, the less polar the compounds, facilitating easier absorption by the nonpolar polyolefins (Nielsen and others 1992b).

**Polymer Characteristics**

**Surface area**

The degree of sorption is directly related to the available surface area in contact with the food (Gremli 1996).

**Polarity**

Different plastic materials have different polarity, hence they differ in their affinity toward the flavor compounds. Flavors are absorbed more easily in a polymeric film of similar polarity (Gallo and others 1999). Polyolefins are highly lipophilic and are incompatible for packaging products with nonpolar substances (such as fats, oils, aromas) since they can be absorbed and retained by the package (Hernandez and others 2001). The polyesters, however, are more polar than the polyolefins and hence show less affinity for the nonpolar components. Table 2 shows the approximate upper and lower limits for partition coefficients one may normally encounter in plastic/food systems based on the polarities of the solutes, plastics, and foods (Baner 2000a). It also shows the approximate ranges of partition coefficient values for various solutes between typical food-contact plastics and liquid phases.

LLDPE and oriented polypropylene (OPP) (both nonpolar) have been shown to easily absorb limonene and myrcene and, to smaller extents, decanal, hexyl acetate, nonanone, carvone, linalool, octanol, and hexanal (Willige and others 2002a). The flavor molecules carvone and limonene have similar structure but limonene is a nonpolar terpene, while carvone is an oxygenated polar terpene. Hence, limonene is absorbed in larger quantity than carvone.

**Glass transition temperature**

Sorption rates to a certain extent depend on the glass transition temperature ($T_g$) of the polymer that determines the flexibility of the polymer molecules. Below $T_g$, the polymer molecules are stiff (glassy state) and the chance of a flavor molecule finding a sufficiently large void is limited. Above $T_g$, the polymer molecules are highly flexible (rubbery state), which makes this chance higher. Table 3 shows the glass transition temperatures of polymers commonly used for food packaging.

Rubbery polymers such as the polyolefins PE and PP, which have a $T_g$ below ambient temperature, have a high diffusion coefficient for flavors with steady-state permeation being established quickly in such structures (Giacin and Hernandez 1997). Stiff-chained polymers that have a high glass transition temperature generally have low permeability, unless they also have a high free volume (Miller and Krochta 1997). Polymers such as the polyesters PET, PC (polycarbonate), and PEN (polyethylene naphthalate) have a $T_g$ above ambient temperature. At room temperature, these glassy polymers have very stiff chains and a very low diffusion coefficient for flavor molecules at a low concentration. Glassy polymers such as polyvinylidene chloride have a low diffusion coefficient for aroma molecules at a low concentration and hence display high flavor-barrier properties (Brody and others 1999).

### Table 1 – Solubility parameters ($\delta$ values)

<table>
<thead>
<tr>
<th>Compound/ polymer</th>
<th>$\delta$ values (H)</th>
<th>Hydrogen-bonding character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl butyrate</td>
<td>8.5</td>
<td>Moderate</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>8.5</td>
<td>Moderate</td>
</tr>
<tr>
<td>Isopentyl acetate</td>
<td>8.0</td>
<td>Moderate</td>
</tr>
<tr>
<td>Ethyl-2-methyl butyrate</td>
<td>8.3</td>
<td>Moderate</td>
</tr>
<tr>
<td>Butyl propanoate</td>
<td>8.8</td>
<td>Moderate</td>
</tr>
<tr>
<td>Hexyl acetate</td>
<td>8.6</td>
<td>Moderate</td>
</tr>
<tr>
<td>Hexanal</td>
<td>8.3</td>
<td>Moderate</td>
</tr>
<tr>
<td>Trans-2-hexenol</td>
<td>8.5</td>
<td>Moderate</td>
</tr>
<tr>
<td>Isopentyl alcohol</td>
<td>10</td>
<td>Strong</td>
</tr>
<tr>
<td>Hexanol</td>
<td>10.7</td>
<td>Strong</td>
</tr>
<tr>
<td>Low-density polyethylene</td>
<td>8</td>
<td>Poor</td>
</tr>
<tr>
<td>Linear low-density polyethylene</td>
<td>8</td>
<td>Poor</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>9.2</td>
<td>Poor</td>
</tr>
<tr>
<td>Polyamide</td>
<td>11.1</td>
<td>Strong</td>
</tr>
<tr>
<td>Polyester</td>
<td>10.7</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

### Table 2 – Approximate partition coefficient values for various plastic/food package systems

<table>
<thead>
<tr>
<th>Substance (i)</th>
<th>Polymer (P)</th>
<th>Food phase (L)</th>
<th>$K_{PL}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonpolar (n-alkane)</td>
<td>Nonpolar (PO)</td>
<td>Very polar (water)</td>
<td>$1 \times 10^5$–$1 \times 10^6$ (40000)</td>
</tr>
<tr>
<td>Nonpolar to middle polarity (d-limonene)</td>
<td>Nonpolar (PE)</td>
<td>Very polar (water)</td>
<td>1200</td>
</tr>
<tr>
<td>Nonpolar to middle polarity (d-limonene)</td>
<td>Nonpolar (PO)</td>
<td>Polar (fruit juices)</td>
<td>400–600</td>
</tr>
<tr>
<td>Middle polarity (ketone)</td>
<td>Middle polarity (PVC)</td>
<td>Polar (ethanol)</td>
<td>10–20</td>
</tr>
<tr>
<td>Middle polarity (ester)</td>
<td>Nonpolar (PO)</td>
<td>Very polar (water)</td>
<td>10–40</td>
</tr>
<tr>
<td>Nonpolar (large n-alkanes)</td>
<td>Nonpolar (PO)</td>
<td>Polar (ethanol)</td>
<td>5.8</td>
</tr>
<tr>
<td>Nonpolar (n-alkane)</td>
<td>Nonpolar (PO)</td>
<td>Nonpolar (n-alkane)</td>
<td>1</td>
</tr>
<tr>
<td>All polarities</td>
<td>All polymers</td>
<td>Oil</td>
<td>0.1–10</td>
</tr>
<tr>
<td>Polar (alcohol)</td>
<td>Very polar (PA)</td>
<td>Very polar</td>
<td>1</td>
</tr>
<tr>
<td>Polar to middle polarity (alcohol and hydrocarbon)</td>
<td>Polar (PET)</td>
<td>Polar</td>
<td>$0.1 – 3$</td>
</tr>
<tr>
<td>Polar (alcohol)</td>
<td>Nonpolar (PO)</td>
<td>Very polar (water)</td>
<td>0.5</td>
</tr>
<tr>
<td>Polar (alcohol)</td>
<td>Middle polarity (PVC)</td>
<td>Polar (ethanol)</td>
<td>0.1 (0.07)</td>
</tr>
<tr>
<td>Polar (alcohol and middle polarity)</td>
<td>Very polar, polar</td>
<td>Polar</td>
<td>$&gt;0.1$</td>
</tr>
<tr>
<td>Very polar (acid)</td>
<td>Nonpolar (PO)</td>
<td>Very polar (water)</td>
<td>0.001 (0.001)</td>
</tr>
</tbody>
</table>
2002). PEN has excellent performance characteristics in comparison to PET for carbonated beverages, allowing hot-fill, rewash, and reuse, due to its high \( T_g \) (VanLune and others 1997).

**Polymer crystallinity**

Morphological properties that influence permeability and diffusivity include structural regularity or chain symmetry leading to 3-dimensional order or crystallinity (Brody 2002). The more ordered the polymer molecular structure, the lower the rate of sorption of the food aroma constituents. Crystalline regions can reduce sorption or act as impermeable barriers for diffusion through the polymer. They can act as crosslinks to prevent swelling of the polymer. The crystalline regions can also restrain polymer segmental mobility affecting the solute permeability to the amorphous regions. Thus, the degree of sorption for a given solute is often related to the degree of the amorphous polymer content (Charara and others 1992; Letinski and Halek 1992). PP is an example of a crystalline polymer that can exist in various degrees of crystallinity.

Absorption of limonene and myrcene by PC is found to be much higher than by PET and PEN, although the \( T_g \) of PC is much higher than the \( T_g \) of PET and PEN. This is attributed to the lack of crystalline regions in PC, which is a totally amorphous polymer (Nielsen 1994).

**Surface polymer hydrolysis**

Surface hydrolysis of ethylene-vinyl acetate copolymer can alter sorption behavior. While the sorption of hydrocarbons, ethyl octanoate, and decanal into hydrolyzed EVA film is depressed, the sorption of alcohols is promoted. This is mainly attributed to solubility of the individual compounds (available from: www.foodproductdesign.com).

**Polymer density**

The amount of aroma compounds sorbed in polymers has been shown to decrease with an increase in polymer density. The sorption rate for limonene decreased from 75% to 63% and that of carvone decreased from 17% to 10% when the PP density increased from 0.8830 g/cm\(^2\) to 0.9213 g/cm\(^2\), respectively (Gremli 1996).

**Free volume of the polymer**

The free volume of a polymer is the molecular “void” volume that is trapped in the solid state (Salame 1989). The permeating molecule finds an easy path in these voids. Generally, a polymer with poor symmetry in the structure or bulky side chains will reduce sorption or act as impermeable barriers for diffusion through the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer. They can act as crosslinks to prevent swelling of the polymer.

**Use of recycled plastics**

In an effort to reduce wastes from food packaging materials, refillable PET bottles for carbonated drinks have been adopted in many countries. A major problem associated with refilling is the sorption of flavors from foodstuffs by the container causing off-flavors in the products filled into the same container. The extent of sorption is dependent on temperature, the polymer type, the carbon chain length, and the type of functional groups of the sorbate. Washing with sodium hydroxide solutions removes less than half the sorbed amount of terpenes from plastic bottles (Gremli 1996). A study to evaluate the efficacy of washing of PET bottles intended for reuse with sodium hydroxide solution in order to remove limonene, linalool, and linalyl acetate showed limonene to be significantly sorbed onto the walls of the bottles even after washing (Safa 1999).

Recycling of old polymers as new bilayer bottles may be of value if a virgin polymer layer is placed between the recycled polymer and the food. The virgin polymer layer plays the role of a functional barrier. In the case of solid foods, the process of contamination by the recycled polymer is controlled by radial diffusion through the bottle and the food. An increase in the volume of the bottle is associated with a decrease in the area of the bottle-food interface per unit volume of food (Rosca and Vergnaud 1998).

**External Factors**

**pH**

\( \text{pH} \) influences the sorption of aroma compounds into the packaging material. \( \text{pH} \) has been shown to affect sorption by a factor of 40 between \( \text{pH} \) 3 and 5 for 2-hexanal into PE (Leufven and Hermansson 1994). Lowering the \( \text{pH} \) to 3 increased the sorption of alcohols into LDPE (Nielsen and others 1992a). Sorption of limonene is shown to be 1.3 times more in LDPE at 22 \(^\circ\)C and at \( \text{pH} \) 5.2 than at \( \text{pH} \) 2.6 (Blain 1994). Nonetheless, a study on limonene in orange juice showed \( \text{pH} \) to have no significant effect on scalping (Nielsen and others 1992a).

Leufven and Hermansson (1994) studied the interaction of aroma compounds such as trans-2-hexanal, 2-heptanone, 6-methyl-5-hepten-2-one, 6-methyl-5-hepten-2-ol, and limonene from tomato juice with polymers such as PET, PE, and EVOH as a function of \( \text{pH} \). The amount of extractable aroma compounds in the different polymers at all \( \text{pH} \) values decreased in the following order: EVOH > PE > PET. Between these polymers, the sorption of the aromas was less influenced by \( \text{pH} \) in PET than in the other 2 polymers, where PE contained larger amounts of the compounds at \( \text{pH} \) 4 than at \( \text{pH} \) 7. For EVOH, there was an increase in sorption of 4-limonene with increasing \( \text{pH} \). Table 4 shows the amount of added aroma compounds sorbed in the polymer films. It is hypothesized that \( \text{pH} \) has a direct relationship with polarity, solubility, and structure of molecules and can be influenced by them.

**Food composition**

Food constituents play an important role in influencing the sorption of flavors. Not only the type of plastic used is of importance for the uptake of aroma compounds, but also the possible interactions between the flavor and food components. Flavor components may be dissolved, adsorbed, bound, entrapped, encapsulated, or retarded in their diffusion through the food matrix by food components. The relative importance of each of these mechanisms varies with the properties of the flavor chemical (functional groups, molecular size, shape, volatility, and so on) and the physical and chemical properties of the components in the food. Proteins, carbohydrates, and lipids interact with flavors, changing the concentration of free flavor in solution and, consequently, affecting their absorption. Absorption of flavor compounds by linear low-density polyethylene (LLDPE) was studied...
The presence of water vapor often accelerates the diffusion of gases and vapors in polymers with an affinity for water. The water diffuses into the film and acts like a plasticizer, opening the polymer structure to molecular transport. The solubility of ethyl propionate in polyvinyl alcohol has been shown to reduce with an increase in RH (Landois and Hotchkiss 1988). This is attributed to the competition between ethyl propionate and water molecules for available sorption sites.

**Storage conditions**

Generally, permeability, diffusion, and solubility coefficients follow a van’t Hoff-Arrhenius relationship, resulting in increased permeation with an increase in temperature (Brody 2002). Since the effect is accentuated at ambient temperatures compared to refrigerated temperatures, the adverse effects have appeared more frequently in foods contained in retort pouches, aseptic packages, and hot-filled flexible packages.

The increased flavor absorption at higher temperatures is due to increased mobility of the flavor molecules; changes in the polymer configuration such as swelling or decrease of crystallinity and changes in the volatile solubility in the aqueous phase (Gremli 1996). In 1 study, the total amount of flavor absorbed increased considerably with temperature from 4 °C to 40 °C, the absorption by polyolefins such as LDPE and OPP being several times higher than by the polyesters such as PC, PET, and PEN, indicating polyesters to be more preferable over polyolefins as packaging materials (Willige and others 2002b).

Storage temperature has been demonstrated to affect the degree of sorption of aromas by PE. Sorption of limonene and myrcene from commercial orange drink stored for 12 wk in PE bottles was found to be 3.40 and 9.90 μg of limonene/g PET and 0.11 and 0.33 μg of myrcene/g PET at 4 °C and 25 °C, respectively. The higher values at 25 °C could be due to the greater mobility of the molecules or more swelling of the polymer generating more space for incorporation of the dissolved molecules (Nielsen and others 1992a; Gremli 1996). Similarly, the solubility coefficient for aldehyde vapors in linear LDPE was maximal at 25 °C, with sorption being lower at both 5 °C and 75 °C (Leufven and Stollman 1992). The sorption of aldehyde vapors by polyvinyl chloride (PVC) also decreased as the temperature decreased. VanLune and others (1997) suggested that the crystallinity of PET decreased

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### Table 4 — Amount of added aroma compound (μg cm⁻²) extracted from polymer films stored in spiked tomato juice

<table>
<thead>
<tr>
<th>Polymer</th>
<th>pH</th>
<th>Days of storage</th>
<th>Trans-2-hexenol</th>
<th>2-heptanone</th>
<th>6-methyl-5-hepten-2-one</th>
<th>6-methyl-5-hepten-2-ol</th>
<th>Limonene</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>4</td>
<td>1</td>
<td>11</td>
<td>20</td>
<td>44</td>
<td>36</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>22</td>
<td>77</td>
<td>12</td>
<td>55</td>
<td>206</td>
</tr>
<tr>
<td>PET</td>
<td>4</td>
<td>1</td>
<td>11</td>
<td>21</td>
<td>8</td>
<td>4</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>22</td>
<td>31</td>
<td>24.4</td>
<td>14</td>
<td>58</td>
</tr>
<tr>
<td>EVOH</td>
<td>4</td>
<td>1</td>
<td>10</td>
<td>8</td>
<td>7</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>14</td>
<td>28</td>
<td>21</td>
<td>11</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1</td>
<td>28</td>
<td>50</td>
<td>50</td>
<td>155</td>
<td>73</td>
</tr>
</tbody>
</table>

---

**Relative humidity (RH)**

The presence of water vapor in model systems representing differences in composition of the food matrix. The extent of flavor absorption by LLDPE was influenced by food components in the order oil or fat > polysaccharides and proteins > disaccharides (Willige and others 2000a). Due to the lipophilic character of many flavor compounds, food products with high oil/fat content tend to lose less flavor by absorption into LLDPE packaging than food products containing no or a small quantity of oil (Willige and others 2000b). The presence of a relative small amount of oil (50 g/L) has been shown to decrease absorption substantially. Also, proteins, particularly, β-lactoglobulin and casein, are able to bind flavors, resulting in suppression of absorption of the flavor compounds. Polysaccharides such as pectin and carboxymethylcellulose increase viscosity and consequently decrease absorption. Disaccharides such as lactose and saccharose increase absorption, probably by a “salt-out” effect of less nonpolar flavor compounds.

Selective flavor sorption by packaging materials constitutes a major problem in beverages packaged in PE that has very high affinity for nonpolar compounds. Since most beverages are water based, the compounds more miscible in PE are absorbed. It is hypothesized that by lowering the solution polarity or creating nonpolar regions (emulsified oil droplets) the equilibrium partition coefficient could be reduced thereby increasing flavor retention. A study to determine whether oil or sucrose in solution, but not sucrose. For compounds most preferentially absorbed by PE, addition of oil could reduce flavor sorption by PE showed that the sorption and partition coefficient of various compounds into PE were greatly influenced by the presence of oil in solution, but not sucrose. For compounds most preferentially absorbed by PE, addition of oil greatly reduced flavor loss, the reduction magnitude being very significant with only 0.1% oil. It is hypothesized that flavors incorporated into an oleoresin could be used to make beverages resistant to flavor scalping (available from: www.foodproductdesign.com).

**Selective flavor sorption by packaging materials constitutes a major problem in beverages packaged in PE that has very high affinity for nonpolar compounds.**
Examples of Specific Flavor Systems with Packaging Materials

Citrus flavors

Citrus flavors, which contribute to the flavor of orange juice, have been the major subject of study with respect to flavor scalping for quite some time. Citrus components from cold-pressed and terpeneless oils have been shown to be absorbed into various polymers such as LDPE, HDPE, PP, and surlyn used in aseptic packaging (Charara and others 1992). Citrus essential oils consist of terpenes, sesquiterpenes, oxygenated compounds, and nonvolatile components while terpeneless oil consists of a higher concentration of oxygenated compounds and a very low concentration of terpenes.

Table 5 shows the percent absorption of flavors from cold-pressed and terpeneless orange oil extracted from 4 polymers using cyclohexane. LDPE has the highest absorption value because of its large amorphous area and low crystallinity, the absorption and diffusion taking place in the amorphous area of the polymer. Terpene hydrocarbons being lipophilic tend to diffuse into the amorphous regions of the polymers. HDPE and PP absorbed constituents to a lesser extent probably due to their higher crystalline structure. About 70% of limonene was lost from cold-pressed orange oil in contact with LDPE for 4 d, while only a 30% loss was observed from orange oil in contact with HDPE and PP. Surlyn was shown to absorb flavor constituents moderately.

Table 5—Percent absorption of components from cold-pressed and terpeneless orange oil (Charara and others 1992)

<table>
<thead>
<tr>
<th>Component</th>
<th>LDPE</th>
<th>HDPE</th>
<th>PP</th>
<th>Surlyn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold pressed</td>
<td>68</td>
<td>30</td>
<td>28</td>
<td>53</td>
</tr>
<tr>
<td>Limonene</td>
<td>68</td>
<td>30</td>
<td>28</td>
<td>53</td>
</tr>
<tr>
<td>Pyrene</td>
<td>58</td>
<td>21</td>
<td>20</td>
<td>49</td>
</tr>
<tr>
<td>Myrcene</td>
<td>66</td>
<td>28</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>Terpeneless</td>
<td>54</td>
<td>22</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>Limonene</td>
<td>54</td>
<td>22</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>Copiene</td>
<td>40</td>
<td>ND</td>
<td>ND</td>
<td>17</td>
</tr>
<tr>
<td>Caryophyllene</td>
<td>34</td>
<td>4</td>
<td>9</td>
<td>19</td>
</tr>
<tr>
<td>Octylacetate</td>
<td>35</td>
<td>ND</td>
<td>13</td>
<td>21</td>
</tr>
<tr>
<td>Undecanal</td>
<td>30</td>
<td>ND</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Dodecanal</td>
<td>22</td>
<td>7</td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>Decanal</td>
<td>18</td>
<td>6</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>Perillaldehyde</td>
<td>10</td>
<td>ND</td>
<td>ND</td>
<td>7</td>
</tr>
<tr>
<td>Geranial</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Linalool</td>
<td>3</td>
<td>&lt;1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
the absorption of d-limonene up to 40% did not affect the sensory quality of orange juice during 3 mo of storage at 20 °C. They suggested that d-limonene contributed scarcely to the flavor of orange juice. Moreover, they considered limonene absorption even as an advantage, since limonene is known as a precursor to off-flavor compounds. They also reported the storage temperature to be the main quality parameter for the shelf life of orange juice.

**Apple aroma compounds**

Evaluation of 10 apple aroma compounds from its aqueous solution showed major differences in the amount of aroma compounds absorbed by the polymers (Nielsen and others 1992b). LDPE, LLDPE, and PP absorbed larger quantities of aroma compounds than did the polar polymers. PP absorbed larger amounts of aroma compounds than the 2 polyethylenes, which may be a consequence of differences in crystallinity and morphology of the polymers. LDPE is reported to possess long-chain branching while LLDPE exhibits short-chain branching, but similar density and equal heat of fusion and degree of crystallinity. Konczal and others (1992) reported larger amounts of apple aromas to be sorbed by LDPE than by EVOH with high ethylene content.

**Migration from Packaging Materials**

Migration is an important safety aspect to be considered when designing food packaging materials. Plastic additives, frequently used to improve polymer properties, and residual monomers or oligomers are not chemically bound to the polymer molecules and can, therefore, move freely within the polymer matrix. Consequently, at the interface between the packaging material and food, they can dissolve in the food product and thus adversely affect the flavor and acceptability of the food (Hernandez and Gavara 1999). Some of the additives that are more likely to migrate are the plasticizers used in a range of plastics, but more particularly in PVC films where they can migrate in PVC food-contact situations (available from: www.foodscience.afisc.csiro.au). While paper and board materials may transmit taint or odor to a food, plastics have a much greater potential to do this. The presence of monomers can contribute to significant off-flavors, styrene monomers at 0.5% in polystyrene (PS) being responsible for the characteristic plastic odor of many packaged foods. Fats and oils in food products, however, can help mask off-flavors from monomers and odorous residues from plastic processing. Nevertheless, as consumers shift toward lower fat products, off-flavors contributing directly via packaging materials may become more of a problem. A number of components of ink may cause unpleasant flavors in food if the manufacture of the packaging material is not carefully controlled. Solvents associated with packaging inks and with resins used in bonding the various layers of laminated packaging films can be absorbed by the product to contribute off-flavors (available from: www.foodproductdesign.com).

The nature and strength of off-odors migrating to the food depend on a number of factors, including the chemical nature of the migrant (its volatility and polarity), the lipophilicity of the food matrix, the physical structure of the food (solid compared with liquid), time/temperature conditions during storage, and the aroma activity (strength) of the migrant (available from: www.foodproductdesign.com). Migration of off-flavors from the packaging material could be a result of plasticizers, inks, and dyes used for graphics or from resins used in the bonding of the package.

Some factors that could affect migration or be a source of undesirable flavors in the final packaged product are described briefly.

**Molecular weight of the migrant**

Migration is a term used to describe the process of mass transfer from a food packaging material to its contents. If one reduces the migration process to the diffusion in and from the plastics, then the migratability of plastic constituents corresponds predominantly to the volatility or molecular weight of these organic substances and to the basic diffusivity of a polymeric type (Franz 2000). For a given plastic, this means that the mobility of a migrant decreases with increasing molecular weight.

**Solubility of the migrant in the food matrix**

Thermodynamic properties such as polarity and solubility influence the migration rate due to interactions between polymer, migrant, and food stimulant (Helmeroth and others 2002). For instance, if a migrant has poor solubility in the food simulant, it will rather remain in the polymer than migrate into the food simulant. This is often the case with nonpolar additives in nonpolar polymers such as LDPE, PP, and PS in contact with more polar food simulants such as water or 3% acetic acid. Higher migration rates are, therefore, often found for fatty simulants such as olive oil, 95% ethanol, or isooctane than for aqueous food simulants (Till and others 1987; Riquet and Feigenbaum 1997; Linssen and others 1998). If the food simulant itself has a high affinity for the polymer, then it may be absorbed by the polymer.

Most of the plastic constituents have a lipophilic rather than hydrophilic character and, therefore, migration increases strongly with increasing fat content and especially so where the fat or oil represents the outer phase of the food matrix (Franz and others 2000). The increase in migration is not necessarily due to an increase in the substance's diffusion coefficient due to interactions between the fat and the plastic as is often assumed (Baner and others 1992). The amount of substances migrating from plastics into foodstuffs with high fat content is higher than in foodstuffs with water content owing to the higher solubility of the migrating organic compounds in fat compared to water. In fact, the higher the fat content of the product, the higher the taste threshold concentration. For styrene, Bruck and Hammerschmidt (1977) developed an equation that relates the fat content of the food product to the taste threshold concentration as threshold (mg/L) = 0.0025 (80 × % fat in food + % water in food). Conversely, water and products with high water content (juices, skin milk) have lower taste thresholds usually on the order of 50 ppm.

**Storage temperature**

At lower temperatures, including refrigeration, migration of plastic components to foods may occur, the migration being much slower than at higher temperatures (available at: http://www.foodscience.afisc.csiro.au).

An understanding of the interactions between food ingredients and polymeric packaging materials requires knowledge of several factors. It is worthwhile to examine the relative balance of the various factors and their overall effect on migration.

**Resins as a source of off-flavors**

Resins used in bonding of paper layers can be a culprit in the migration of off-flavors in packaged foods. Quaker Oats Co. discovered a piney/spruce off-flavor in packaged ready-to-eat cereals (available from: www.foodproductdesign.com) that contributed an uncharacteristic flavor note to the cereal. When the packaging material used for the outer boxes was examined, it did not possess a piney odor, but the inner glassine liner contained a strong piney odor. The liner was composed of 2 sheets of Kraft paper laminated with a resin in microcrystalline wax and over-waxed on both sides with paraﬃn wax.
Odors from inks and dyes

Residual solvents from inks and dyes used for packaging graphics can cause off-flavor problems in foods (available from: www.foodproducedesign.com). A nondairy coffee creamer manufacturer noticed shipping boxes of foil-wrapped nondairy creamer to have a severe musty odor. Results showed that all of the new production samples contained the odor problem and had a peak identified as 1,3,5-trimethylbenzene (mesitylene). The trimethylbenzene peak had a strong musty odor identical to the odor of contaminated boxes. Further checking revealed that the packaging supplier had used a new type of ink containing high levels of 1,3,5-trimethylbenzene for graphics on the foil packets.

Inks and model ink components incorporated deliberately into carton boards at low temperature and during microwave heating have shown benzophenone to migrate to the packaged food even from PE-coated boards, attributed mainly to the permeability of PE to low-molecular-weight substances (Johns and others 2000). Migration of benzophenone, benzyl butyl phthalate, butyl benzocate, chlorodecane, and dimethyl phthalate was also detected after storing the food at –20 °C for 1 wk in the impregnated carton-board. It was concluded that for inks used to print food-contact materials, the content of low-molecular-weight volatiles should be controlled to lower the migration levels.

Off-odors from polyamide/ionomer laminates

An off-odor with a smell of cat urine is reported to have occurred in cooked ham products packed in polyamide/ionomer laminate films (Piringer and Ruter 2000). A gas chromatograph (GC) study of such products was able to identify the presence of diacetone alcohol (DAA), which was used in the printing ink of the film that subsequently migrated into the laminate. Degradation reaction of DAA by the ethylene ionomer resulted in the formation of 4-methyl-4-mercaptopentane-2-one off-odor. It is proposed that when printing ionomer films or laminates containing ionomer in which foods with sulfur-containing proteins are packed, the absence of mesityloxide and its chemical precursors such as acetone and diacetate alcohol must be guaranteed.

Styrene taint in dairy products

An example of a product that has had styrene taint problems over the years has been dairy products such as coffee creamers and condensed milk packed in thermoformed PS single-serve carton boards at low temperature and during microwave heating. There have shown benzophenone to migrate to the packaged food even from PE-coated boards, attributed mainly to the permeability of PE to low-molecular-weight substances (Johns and others 2000). Migration of benzophenone, benzyl butyl phthalate, butyl benzotate, chlorodecane, and dimethyl phthalate was also detected after storing the food at –20 °C for 1 wk in the impregnated carton-board. It was concluded that for inks used to print food-contact materials, the content of low-molecular-weight volatiles should be controlled to lower the migration levels.

Sorption

High-pressure food processing. Single-layer and multilayer plastic structures can be used in combination with high-pressure processing (HPP) without concern that the process will enhance sorption. In 1 study, sorption behavior and flavor scaling potential of selected packaging films in contact with food simulants (FSL) (ethanol and acetic acid solutions) were evaluated after high-pressure processing (Caner and others 2004). HPP treatment (800 MPa, 10 min, 60 °C) showed d-limonene concentration in the films and food simulants to be insignificantly affected by HPP, except for the metallocene PET/EVA/LLDPE in comparison to the control pouches, which were exposed to atmospheric pressure at 60 °C for 10 min in an electric oven.

Irradiation. Recently, irradiation has been explored as a viable means in the shelf life extension of many foods. Apple cider packaged in 3 plastic polymers, PS, LDPE, or nylon-6 (N6), and irradiated at 2 kGy was compared with unirradiated cider packaged
in glass containers (Crook and Boylston 2004). The extent of flavor absorption by the packaging materials was influenced by the polarity of the polymer and the flavor compound, with plastic polymer having a greater affinity for compounds with similar polarity. Cider irradiated and stored in PS containers was shown to have a lower rate of loss than untreated cider or irradiated cider packaged in LDPE for volatile flavor compounds characteristic of the apple or fruity taste and aroma.

**Migration**

**Microwave treatment.** In the microwave oven, plastic containers and wraps are often warmed to a point that plasticizers are released from the plastic into the food (Bishop and Dye 1982). Numerous studies indicate that some plasticizers can cause undesirable side effects in animal tissue, and that the amount of migration could be as high as 23% of the total weight. In 1 study, migration of plasticizers such as dioctyl adipate (DOA) from plasticized PVC and acetyltributylcitrate (ATBC) from polyvinylidene chloride (PVDC/PVC) (Saran164) films into ground meat heated for 4 min was found to be 84 mg/kg (14.7 mg/dm²) and 95.1 mg/kg (2.5 mg/dm³), respectively (Badeka and Kontominas 1998). Such migrations could result in deterioration of the final food quality, posing off-flavor and/or safety problems. The migration of compounds from a polymeric material into a food-contacting phase would depend on several factors such as the nature and thickness of the packaging material, the nature of the food in contact, initial concentration of additives in the polymer, compatibility of the additive/polymer system, temperature, time of contact, and others.

One development in food packaging that has received much attention lately is the microwave susceptor, a package developed to meet consumer demands for convenience and quality in microwaveable food products. A susceptor is typically a piece of polyester film that has been metallized with aluminum laminated either to paperboard or between 2 layers of paper. Food/package interactions that result from the use of microwave susceptors and dual ovenable trays have been extensively studied by the U.S. Food and Drug Administration (FDA)’s Indirect Additives Laboratory. Susceptors are typically constructed of plastic such as PET, adhesives, and paper, and temperatures in excess of 212 °F are common for such packaging. At elevated temperatures, both volatile and nonvolatile chemicals from the package can migrate into foods (Hollifield 1991). Generally, the more paper in the susceptor construction, the greater the amount and number of volatile substances released on heating. The number of substances released at levels greater than 0.5 μg/inch² of susceptor surface from susceptors containing acrylic-based or vinyl-acetate-based adhesives includes acetone, methyl vinyl ketone, pentanal, toluene, hexanal, furfural, heptanal, benzaldehyde, nonanal, furan, isobutanol, acetic acid, butanol, octanal, styrene, octyl acetate, 5-hydroxymethylfurfural, and crotonaldehyde (Hollifield 1991).

**Irradiating radiation.** Irradiation for the control and reduction of spoilage by the packaging materials was influenced by the polarity of the polymer and the flavor compound, with plastic polymer having a greater affinity for compounds with similar polarity. Cider irradiated and stored in PS containers was shown to have a lower rate of loss than untreated cider or irradiated cider packaged in LDPE for volatile flavor compounds characteristic of the apple or fruity taste and aroma.

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One development in food packaging that has received much attention lately is the microwave susceptor, a package developed to meet consumer demands for convenience and quality in microwaveable food products. A susceptor is typically a piece of polyester film that has been metallized with aluminum laminated either to paperboard or between 2 layers of paper. Food/package interactions that result from the use of microwave susceptors and dual ovenable trays have been extensively studied by the U.S. Food and Drug Administration (FDA)’s Indirect Additives Laboratory. Susceptors are typically constructed of plastic such as PET, adhesives, and paper, and temperatures in excess of 212 °F are common for such packaging. At elevated temperatures, both volatile and nonvolatile chemicals from the package can migrate into foods (Hollifield 1991). Generally, the more paper in the susceptor construction, the greater the amount and number of volatile substances released on heating. The number of substances released at levels greater than 0.5 μg/inch² of susceptor surface from susceptors containing acrylic-based or vinyl-acetate-based adhesives includes acetone, methyl vinyl ketone, pentanal, toluene, hexanal, furfural, heptanal, benzaldehyde, nonanal, furan, isobutanol, acetic acid, butanol, octanal, styrene, octyl acetate, 5-hydroxymethylfurfural, and crotonaldehyde (Hollifield 1991).

**Ionizing radiation.** Irradiation for the control and reduction of microorganisms and insects and the extension of product shelf life has become a potential preservation technique in many countries. Several researchers have studied migration into food simulants, describing it to be a consequence of irradiation. Lox and others (1991) found an increase in migration as a function of dose up to 10 kGy and a decrease at higher doses from extruded PVC irradiated with 3 to 25 kGy γ-rays. With accelerated electrons, the migration increased steadily with the absorbed dose. However, no significant migration was observed with LDPE and PP at absorbed doses of up to 25 kGy with either electron irradiation or a cobalt-60 γ-source (Rojas and Pascat 1990).

The gas permeability of LDPE, HDPE, PET, and PVC packaging materials is unaffected by irradiation doses of up to 8 kGy (Buchalla and others 1993). However, irradiation of these polymers can result in the release of hydrogen, CO₂, CO, and methane gases and the formation of volatile oxidation products, including peroxides, alcohols, aldehydes, ketones, and carboxylic acids. Flexible food packaging materials (LDPE, EVA, PET/PP/EVOH/PE) irradiated with low (5 kGy, corresponding to cold sterilization), intermediate (20 kGy), and high (100 kGy) doses produced these volatile compounds in amounts that increased with increasing irradiation dose (Riganakos and others 1998). The extent of radiation-induced changes depends on many factors such as the type of polymer, processing exposure, and irradiation conditions (Buchalla and others 1993). Odor intensity values for various polymers have been reported by Trapp (1959). More intense odors on irradiation were observed in LDPE than in HDPE, developing stronger off-odors than PS and various polyamides and polyesters. The intensity of off-odors of irradiated PE was found to increase with oxygen concentration in the atmosphere with a good correlation existing between the amount of products formed by irradiation and the intensity of off-odor (Azuma and others 1984). The odor-producing volatiles from LDPE films irradiated with a dose of 20 kGy from a 2.5 MeV electron beam were identified to be mainly aliphatic hydrocarbons, aldehydes, ketones, and carboxylic acids.

Migration studies with 9 different polymers irradiated at 60 kGy showed increased migration into distilled water for polyamide-6, polyvinyl chloride-vinyl acetate, and poly(vinylidene chloride-vinyl chloride) after γ-irradiation (Killoran 1972). The extracted substances were identified as low-molecular-weight materials of the polymers and, in the case of PVC, as an ester-type plasticizer. Transfer of off-odors from 2 laminates (with LDPE and HDPE as inner layers) into water was evident at the lowest dose applied (10 kGy) and increased with the absorbed dose to reach a maximum at 150 kGy; however, during storage, the off-odors gradually disappeared. Nevertheless, polyester-aluminum-HDPE did not produce any off-odors up to 500 kGy.

**Rerouted foods.** Migration from multilayer laminated film pouches intended for rerouted foods was investigated using HPLC analysis, a fluorescence detector, and measurements of residue on evaporation, consumption of potassium permanganate, and total organic C (Uematsu and others 2005). HPLC analysis revealed that the levels of migrants in oil and water heated in the pouches (121 °C, 30 min) were 10 times those in the corresponding official simulants, n-heptane (25 °C, 60 min), and water (95 °C, 30 min). Bisphenol A diglycidyl ether and related compounds were found in oil and water heated in the pouches, as well as in the official simulants. Results indicate that these compounds were present in the adhesive between the laminated films and migrated through the food-contact film of the package.

**Analytical Techniques**

**Sorption of food flavors**

In the quantitative analysis of flavor sorption by packaging materials, solvent extraction of flavor compounds is generally followed by determination of the extract concentration by GC (Imai and others 1990). Increasing the extract concentration by distillation or vacuum evaporation is usually used to increase the sensitivity of measuring low-magnitude sorption (Kwapong and Hotchkiss 1987). Solvent extraction and multiple headspace extractions using a purge and trap injector (MHE-PTI) can also be used to study sorption. While the solvent extraction step is highly tedious and time consuming, the MHE-PTI is more convenient, rapid, fully automated, and suitable for volatile aroma compounds.

The techniques currently employed in the evaluation of flavor sorption include GC-MS (mass spectroscopy) analysis using static
headspace sampling, dynamic headspace sampling, and solidphase microextraction (SPME) (available from: www.foodproductsdesign.com, Paik 1992); solvent extraction coupled with GC (Shimoda and others 1988; Imai and others 1990; Nielsen and others 1992a); electronic nose (available from: www.foodproductsdesign.com), supercritical fluid extraction (SFE) coupled with GC (Nielsen and others 1991; Johansson and others 1993); and vacuum microgravimetry (Roland and Hotchkiss 1991).

A novel method developed by Nielsen and others (1991) using supercritical carbon dioxide extraction directly coupled to GC might prove essential in the continuous investigation of absorbed food components in plastic packaging materials. It is based on the advantageous properties that carbon dioxide has at a pressure and temperature above the critical point when the carbon dioxide is in the supercritical stage. Leufvén and Hermansson (1994) used SFE with carbon dioxide to extract aromas from film samples and deposit them in a chemical adsorbent for thermal desorption onto a GC-FID (flame ionization detection) capillary column. Nielsen and Jägerstad (1994) also used SFE to strip the polymer off the sorbed volatiles, which was then deposited directly onto a GC-FID capillary column for elution. These SFE techniques are limited to aromas that are soluble in the given supercritical fluid (Nielsen and others 1991).

In a study on the interaction of orange juice with inner packaging material of an aseptic product, the volatile components absorbed by the inner packaging material were extracted by ether and analyzed by GC-MS (Jeng and others 1991). The empty pack, after rinsing with deionized water and air-drying, was filled with the polymer resulting from compound sorption and the pressure inside the vessel were recorded by means of a computer. This rapid test for gauging the absorption of volatile compounds. In a study to measure scalping of limonene by LDPE, the LDPE test film was mounted on a YSI 5331 OE. The probe was then placed in the headspace of a flask that contained the selected volatile at the test temperature (Sadler and Braddock 1991). Absorption-induced changes in the readings were monitored on a strip chart recorder. When stable permeation readings indicated maximum absorption, the probe was withdrawn and placed in an air stream equilibrated to the test temperature. As the air stream forced the polymer interactions at flavor concentrations and amounts that are usually encountered in foods.
In a method based on weight change in order to study the absorption of citrus flavor volatiles by LDPE, tarred LDPE sheets were stored in a closed desiccator over a 50-ml pool of the selected volatile (Sadler and Braddock 1991). After 1 wk, the samples were removed, weighed, and desorbed in a forced-air stream. Weight loss was recorded every 15 min until the polymer was within 5% of its weight prior to volatile treatment. The solubility of the volatile in the polymer was calculated as:

\[
\frac{(A - B)}{B} \times 100
\]

where \(B\) represented the polymer weights before and after volatile absorption.

Cava and others (2005) analyzed the diffusion behavior of limonene in LDPE as a function of sample thickness, permeant concentration, and the outer medium by transmission Fourier transform infrared (FT-IR) spectroscopy. A surprising reduction in diffusion \(D\) and permeability \(P\) coefficients with reducing film thickness was observed, most likely attributed to the morphological differences arising during cast film extrusion. Moreover, the limonene desorption kinetics were found to slow down considerably when desorption of the volatile was carried out in water compared to desorption in air. Finally, the sorption kinetics of limonene in LDPE were found to be much slower when the polymer was put in contact with pressed orange juice (similar to a real packaging case) than when it was put in contact with the pure volatile. A remarkable finding arising from this work is that the diffusion coefficient of limonene in LDPE can vary by up to 2 orders of magnitude depending on the testing conditions, mainly limonene concentration but also polymer morphology, and, consequently, these observations may well account for the extensive variability reported for this permeant in the existing literature.

**Migrants from packaging materials**

With regard to migration, the control of transfer from plastic packaging materials into foods is based on the measurement of the substance in the food or simulant. The direct migration measurement consists of measuring either directly in foodstuffs or more commonly mimicking as closely as possible a given food packaging application using food simulants. The semi-direct migration test applies more severe test conditions by using volatile solvents with strong interactions toward the plastic to enhance the migration rate from the plastic. Thus, the extraction test is based on accelerated mass transport mechanisms where the diffusion coefficients of migrants are increased by several orders of magnitude compared to the original migration test. As a rule, extraction tests are designed such that they make use of the following principle: polar polymer + polar migrant + polar solvent = worst case = nonpolar polymer + nonpolar migrant + nonpolar solvent (Franz and others 2000).

When an off-odor problem occurs and is suspected to be packaging related, it is suggested that the packaging supplier be approached to find out the nonproprietary aspects of the components used during manufacture. The next step is to obtain an analytical profile of the product, typically done using dynamic headspace GC/MS, while simultaneously conducting taste and odor evaluation. To confirm that the off-flavor problem is indeed packaging related, a control should be run where the product is stored using a relatively inert barrier such as glass. Finally, one needs to look for volatiles that correlate with the defect and find their threshold levels. If off-flavor increases over time, then it would be best to look for alternative packaging materials or packaging materials with different barrier compositions.

In general, the first stage in the determination of the migrants in polymers is their separation from the matrix. When the migrant is a volatile compound such as styrene, the headspace GC technique is very suitable for the analysis; it has been used in the EU project Specific Migration by heating the PS dissolved in xylene or dioxane at 90 °C for 120 min. If the migrant is a nonvolatile compound it is essential to use a liquid extraction technique. The solvent used should both dissolve the target compound and also swell or dissolve the polymer matrix. When the polymer is dissolved in a solvent, the polymer is then usually reprecipitated by addition of a solvent in which the polymer is insoluble.

Usually, extraction procedures are carried out with hand shaking (Garcia and others 2006). Nevertheless, sometimes ultrasonics (Marque and others 1998) or maceration (Monteiro and others 1998) could be employed to improve the process. Gramshaw and Vandenburg (1995) used dynamic headspace to extract styrene from thermoset polyester passing through the U-tube nitrogen at 25 ml/min and heating the oven at 200 °C. To analyze styrene dimers and trimers, Soxhlet extraction with dichloromethane was used, followed by size exclusion chromatography to clean up the dichloromethane extracts.

Chromatographic separations in the gas and liquid phases are currently state of the art (Brandsch and others 2000). In the automatic PTI coupled to a GC used for the dynamic MHE of volatile compounds from aqueous solutions as well as films, trapped volatiles after the purge time are thermally flash desorbed and directly injected onto the GC column (Feigenbaum and others 1998). In 1 study, the source of an off-odor in premiums intended for use with dry mix beverages was evaluated in accordance with the ASTM F 151-86 (ASTM 1986) method using headspace GC/mass spectrometry (Apostolopoulos 1998). The premiums were placed in Mason jars which were sealed with Teflon-lined lids, equipped with sampling ports. The Mason jars containing the premium samples were placed inside a mechanically convected oven and heated at 110 °C for 90 min to ensure vaporization of the premium residuals into the headspace of the Mason jars. Using a preheated gas-tight syringe to avoid condensation of the volatiles, headspace aliquots of 1 ml were withdrawn from the Mason jars and injected into GC-MS, equipped with a CP-Sil 8 CB chromatographic column operated at 20 °C for 2 min and then increased at 10 °C/min to 250 °C. The compounds present in the injected aliquots were separated in GC-MS scans with mass spectral identifications. GC-MS was also used in the identification of volatiles produced during electron beam irradiation (Riganakos and others 1998). About 1.2 to 1.6 g of packaging materials was weighed into glass headspace vials, sealed, and irradiated. Helium gas at a flow rate of 30 ml/min was passed for 20 min through the headspace vials maintained at 80 °C. The volatile compounds were collected on a Tenax GC plug filled into the glass liner of an Optic PTV-Injector.

The headspace gas chromatographic (HSGC) method for determining volatile substances emitted from high-temperature food packaging is used to screen microwave susceptors and fatty food simulants (McNeal 2000). Levels of butadiene in a food or food simulant are usually determined by HSGC with automated sample injection and by FID (Franz and others 2000). HS-SPME coupled to GC-electron capture detection can be used for the direct determination of chloroanisoles in wine samples (Urunuela and others 2004).

Additional selective methods of considerable importance include direct mass spectrometry using an electro-spray-ionization (ESI) or atmospheric pressure ionization (API) ion source, which can quickly provide data for several species migrating into a simulant in 1 run. The ESI-MS is especially well suited for complex nitrogen-containing and phenolic structures; combinations of HPLC with ESI-MS or AI-MS also provide a very powerful tool. An analytical procedure based on headspace GC and mass selective detection is usually used to determine volatiles whereas HPLC
with UV detection is quite suitable for determining potential migrants of high molecular weight such as PET oligomers and adhesive plasticizers arbitrarily classified as nonvolatiles (Hollifield 1991).

Total migration of components from packaging materials into fat-releasing foodstuffs is based on the determination of the weight of a sample of the packaging material before and after its storage in a test fat under standard conditions, a correction being applied for the residual fat retained in/on the sample (Figgie and others 1978). The latter may be determined by physical or chemical methods, the calculation being based in most cases on a single component of the triglyceride mixture that has migrated into the sample. With most test fats, differential migration of the individual components of the fat into and incomplete extraction of the absorbed fat from the test polymer are serious sources of error. Fewer problems are associated with the use of 14C-labeled HB 307 as the fat simulant suitable for all types of plastics, including the highly crosslinked and insoluble types.

A reference material for the determination of overall migration from a plastic coextrudate into the fatty food simulant olive oil was produced and certified in an interlaboratory study (Lund and others 2000). The analyses were carried out according to the ENV 1186 standard from the European Committee for Standardization (CEN) with exposure of the coextrudate to olive oil for 10 d at 40 °C. After an initial preliminary interlaboratory study, 8 laboratories participated in the certification round, and 2 different methods were used to obtain single-sided exposure of the plastic to the oil. A reference value of 8.6 mg/dm² to 1.4 mg/dm² (half width of the 95% confidence interval) was obtained, which is within the range relevant for the regulatory limit (10 mg/dm²), making this reference material suitable for laboratories measuring according to the EU overall migration limit.

A neutron activation method developed for the analysis of HDPE, LDPE, PP, PET, and PS food-contact plastics provides for determination of over 50 elements at a concentration of below 1 mg/kg (Thompson and others 1996). This technique has now been extended to study migration from food-contact materials into standard food simulants (olive oil, acetic acid, ethanol, and water). Samples of plastic are irradiated in a thermal neutron flux to produce radionuclides of the elements present in the plastic. Over a period of time, the radionuclides of these elements may travel from the plastic into the food simulants, and hence migration can be determined. Gamma ray spectrometry performed on the simulants at the end of the test is used to quantify the migration, any activity being attributed to the migration of radionuclides of elements in the plastic. Detection limits of about 0.002 mg/kg were achieved for antimony (Sb) in retail PET bottles.

It is imperative that every analytical method adopted for migration studies be capable of reaching the required detection limit, typically 50 parts per billion or less (Buck and Bussey 2002). To verify whether the methodology is capable of delivering the correct results, FCN (Food Contact Notification) rules state that each analytical method be validated. Extracts of samples or controls must be spiked with the potential migrant at known levels and then analyzed using the same method applied to the sample extracts. Adequate recovery of the spiked material shows that the method works as reported. While chemical analysis guides the search for off-flavor contributors in a food, identifying these also requires sensory evaluation tools.

Legislation

A major concern in packaging is whether the packaging components will migrate into the food product. In addition to concerns about the safety of a packaged food, packagers must also address concerns about whether the packaging will affect appearance, flavor, odor, and other factors influencing consumer acceptance. According to FDA regulations, any packaging material that comes in contact with food must receive FDA clearance before it can be used (Buck and Bussey 2002). While consumer acceptance issues will determine the success or failure of a given product, unsafe packaging is a public health issue and will affect the future of the food and packaging manufacturers. Package component migration can result in food adulteration, which violates government laws, and food safety professionals must be aware of regulations pertaining to this area. The major purpose for performing migration studies is to estimate exposure to food packaging components (Begley 2000). Exposure is calculated to determine an estimate of daily intake (EDI). The EDI for a particular migrant is compared with the acceptable daily intake (ADI) of the migrant, as determined by FDA toxicologists.

In addition to positive lists and SMLs, general provisions have been introduced under the European Community Directive controlling the suitability of materials and articles on the basis of overall migration limits. Also, European Council Directive 82/711/EEC, as amended by European Commission Directive 93/8/CEE (European Commission 1993) establishes in Article 3 that “verification of compliance of migration into foodstuffs with the migration limits shall be carried out under the most extreme conditions of time and temperature foreseeable in actual use.” Time and temperature are 2 factors that affect the migration of substances from plastic materials, in addition to other factors such as compression,-stacking, or vacuum packing that should be taken into account when carrying out migration tests under the worst foreseeable conditions. The transfer of substances is regulated by 2002/72 with 2 different migration limits, that is, overall migration limit and SML. The overall migration limit, the total quantity of substances released by the sample, is 60 mg/kg or 10 mg/dm². Some substances are also regulated with SML, because toxicological data submitted to the Authority are limited or its impact in higher transfer level is considered to be a concern. SMLs are mentioned in Annex II of 2002/72/EC.

The Plastic Materials and Articles in Contact with Food Regulations, 1998, set an overall migration limit for all food-contact plastics, the limit being 10 mg/dm² of plastic surface area, in general. However, a limit of 60 mg/kg of food applies specifically in the case of containers or similar receptacles with a capacity between 0.5 L and 10 L, or which have a contact area that cannot be determined, and for sealing devices such as caps, gaskets, and stoppers (available from: www.food.gov.uk). The Australian Food Standards Code has set maximum migration levels for 3 specific monomers, vinyl chloride, acrylonitrile, and vinylidene chloride, because of their known potential toxicity (available from: www.foodscience.afisc.csiro.au).

A packaging material with the exception of this plastic, water in contact with it can produce characteristic flavor changes. The description of the PE odor ranges from candle-like, stuffy, musty to soapy, to rancid. For this reason, PE used for food applications has high-quality standard requirements. Another packaging material, for which toxicity and safety have been extensively studied is styrene, which is reported to have no health consequence at the levels commonly found in foods. The current European legislation sets no SMLs for styrene in food, which means its content cannot be determined, and for sealing devices such as caps, gaskets, and stoppers (available from: www.food.gov.uk). The Australian Food Standards Code has set maximum migration levels for 3 specific monomers, vinyl chloride, acrylonitrile, and vinylidene chloride, because of their known potential toxicity (available from: www.foodscience.afisc.csiro.au).

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Approaches to the Reduction of the Scalping Process

Judicious selection of polymers is the best way to reduce scalping by the use of crystalline polymers, polymer blends, or edible films (Gallo and others 1999). Fluorination of polymer surface and inert coatings on the polymer surface is yet another approach. Some of the common measures to prevent the scalping process, thus maintaining the integrity of the packaged food items, are described below.

Flavor encapsulation

Protection mechanisms designed into commercial flavor delivery systems provide for release of the flavor at the appropriate time. Advances in encapsulation technology allow encapsulation of hydrophobic or hydrophilic flavors, which are available in a range of particle size, shape, and solubility. Flavors can be encapsulated to protect them from undesirable interactions with the components and the package. The industry is developing micro- and macroencapsulation technologies utilizing various coatings such as polymers, waxes, fats, starch, hydrogenated vegetable oils, proteins, maltodextrines, mono- and diglycerides, gum arabic, alginates, gelatin, and cellulose compounds (available from: www.foodproductdesign.com).

Electron beam irradiation

Electron beam irradiation of ethylene vinyl acetate copolymer films is shown to markedly depress the sorption of flavor compounds such as hydrocarbons and low-polarity compounds (Matsumoto and others 1990). This effect is attributed to the radical reactions evolving changes in the structural characteristics such as crosslinking and scission reactions (Lawton and others 1960).

Selective scalping

Few researchers have addressed how scalping, particularly selective scalping, can improve the flavor profile of food systems. Polymer blends included with an agent that has an affinity for specific compounds can be used to proactively remove deleterious substances in a packaging environment (Del Nobile and others 2002).

The possibility to trap degradation products (produced by chemical reactions) with scavengers such as a zeolite additive or antioxidants and hence prevent degradation products from migrating to the polymer film surface and further into food in contact with the film was investigated by Anderson and Forsgren (2005). Adsorption of oxidative degradation products in a zeolite additive or protection of LDPE by using antioxidants could prevent off-flavor in the packed product, such as water.

The migration of low-molecular-weight compounds formed during polymerization, processing, and forming of packaging materials could be a problem. For example, acetaldehyde is formed in the polyester PET by the thermal decomposition of the ethylene glycol hydroxyl terminal group and the main chain of the polymer (Kagarashi and others 1989). In their study, poly (m-xylene adipamide) (nylon MXD6), D-sorbitol, and α-cyclodextrin aldehyde-scavenging agents were blended with poly (ethylene terephthalate) and thermally pressed into films. The total amount of aldehydes sorbed by the films was 2 to 10 times higher for films containing the aldehyde-scavenging agents than non-blended films. Aldehyde-scavenging films demonstrated selective scalping, preferably for smaller-molecular-weight aldehydes.

Odor absorbent packaging can also be used in combination with base polymers such as PET, LDPE, and PP to eliminate off-odors produced during long-term storage (Perchonok 2003). The odor-producing compounds targeted could be aldehydes and ketones associated with lipid oxidation and cooked odors. Ketones are found in beverages and foods such as ultra-high temperature (UHT) milk. The use of polymeric amines in packaging to remove volatile food components may be an effective means to remove unpleasant flavor notes since ketones and aldehydes contain functional carbonyl groups that readily react with amines.

Choice of packaging material

The choice of plasticizers must be made on the basis of the film’s end use. A possible approach to reduce the potential for migration of plasticizers from PVC into foods is to replace monomeric with polymeric plasticizer compounds of higher molecular weight with reduced tendency for migration due to limited mobility in the polymer matrix, for example, a polyadipate ester-type plasticizer used at 70% level for low-molecular-weight PVC or 50% level for a high-molecular-weight PVC (Demetzis and others 1990).

Vinylidene chloride polymers. Vinylidene chloride polymers are often used in connection with other structural polymers as a barrier to prevent the entry of oxygen into food containers and to limit flavor scalping during long periods of storage. Although these polymers display outstanding characteristics for use in food packaging, they suffer from sensitivity to thermal treatments, undergoing heat-induced degradative dehydrochlorination at processing temperatures of 150 ± 170 °C. To scavenge evolved hydrogen chloride and thus prevent the formation of metal halides by interaction with extruder walls, these materials are usually blended with a small amount of passive base prior to processing (Howell and Uhl 2000).

Biobased food packages resistant to scalping. In general, plastic materials are not inert and where direct contact between the packaged product and the plastic container occurs, there can be migration of substances into the product. The amount of any component that migrates into food depends on the original concentration of the particular component in the polymer and its solubility as well as the temperature, mechanical stresses, and contact time. Therefore, there is a considerable interest in replacing some or all of the synthetic plastics by biodegradable materials in many applications.

Polyactic acid (PLA) has finally arrived as an alternative to PET, PVC, and celluloses in some high-clarity packaging roles. PLA, an aliphatic polyester featuring high-clarity, gloss, stiffness, and easy processing, is fabricated by polymerizing lactic acid monomer (LA) produced by carbohydrate fermentation of corn dextrose. Currently, PLA is being used as a food packaging polymer for short-shelf-life products with common applications such as containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages (Ikada and Tsuji 2000).

The novel resin is forging roles in thermoformed cups and containers and also single-serve drink bottles. Synthesized from processed corn, a renewable plant feedstock, it biodegrades after use, if composted. PLA synthesis requires 30% to 50% less fossil fuel than polymers synthesized from hydrocarbons and thus reduces carbon dioxide emission. These “green” benefits could provide users with a marketing edge. Nonetheless, PLA faces hurdles, including its high density (1.25 g/cc) relative to PP and PS. It also has high polarity, making it difficult to adhere without tie-layers to nonpolar PE and PP in multilayer structures. But the greatest stumbling block is PLA’s cost, currently an average of $1.30/lb. Notably, PLA delivers a balance of properties that has generated enthusiastic interest from some end users. A good example of PLA’s early success is a biaxially oriented PLA (BOPLA) film made by Mitsubishi Plastics in Japan. This BOPLA film is laminated to paperboard in a golf-ball package for Dunlop Japan. The reverse-printed PLA film becomes the clear viewing window when a panel is die-cut out of the paperboard. BOPLA film laminates easily and justifies Dunlop’s “recyclable-compostable” claims.
PLA and PHB (polyhydroxy butyrate) bottles or cups could be used for packaging fresh unpasteurized orange juice (Haugaard and Festeersen 2000). PLA cups have relatively low water vapor permeability and high resistance to scalping compared to PE. Since PHB has a much lower oxygen transmission rate than PLA (Krochta and De Mulder-Johnston 1997) and PHB has high water resistance (Hanggi 1995), coating of PLA with PHB is expected to give a useful biobased packaging material for beverages. Packaging materials based on 100% PHB are also expected to be useful for beverages.

One major concern for biobased packaging materials is that they are moisture-sensitive. To assure food safety, it is advised that these packages be tested under the worst condition of 100% RH for the full anticipated shelf life.

Recently, the application of the nanocomposite concept was shown to be a promising option to improve mechanical and barrier properties of packaging films (Avella and others 2005). Nanocomposite films were obtained by homogeneously dispersing functionalized layered silicates (clay minerals) in thermoplastic starch via polymer melt processing techniques. These films were made by using different starch matrices such as potato starch and a mixture of potato starch with biodegradable polyester. In the case of starch/clay nanocomposites, a good intercalation of the polymeric phase into clay interlayer galleries, together with good mechanical parameters such as modulus and tensile strength, was obtained. Moreover, the conformity of the starch/clay nanocomposite films with actual regulations and European directives on biodegradable materials assessed demonstrated that these materials could be utilized in the food packaging sector owing to their low overall migration limit.

Packaging for wines and liquors. Closure types vary considerably in scalping properties and may cause considerable changes in flavor concentration in wines (Capone and others 2003). Closures tested included screw caps, natural cork closures, a technical cork closure, and 7 synthetic closures. Semillon wine samples spiked with various aroma compounds, including pyrazines, oak-related phenols, ethyl esters of fatty acids, monoterpenes, or hydrocarbons, and sealed with the closures under test were stored for 2 yr. No absorption of any of the flavor or aroma compounds on the screw caps was observed. Relatively nonpolar compounds were absorbed by cork or synthetic closures. The more polar compounds were not absorbed by any of the closures. For the nonpolar compounds, absorption was greatest for the synthetic closures; technical cork closures performed similarly to the natural corks, but had a slightly higher absorption capacity.

For pale ale bottled in clear PET and PEN containers with plastic caps, and a glass control bottle with a crown closure, sensory, and physicochemical properties at the 14th wk, showed PEN bottles to have provided the best protection, followed by glass and finally PET (Goodrich 1997).

Packaging for aseptic foods. Aseptic foods are packaged in a variety of polymeric materials. The PE liner in brick type aseptic containers scalps d-limonene, geranial, octanal, and decanal from juice products (Arora and others 1991). As a result, the packaged fruit juice lacks flavor notes characteristic of fresh juice. There are reports of 62% and 37% sorption of nonpolar and polar organics, respectively, by PP. PP is ranked second after PE in the quantity of flavor compound sorbed. Juices packed in co-extruded PP containers, consisting of PP outer and inner layers surrounding an internal EVOH layer, have shown a marked decrease in d-limonene content compared to juices packed in foil containers due to sorption. A layer of Saran is suggested with PP and HDPE to reduce the sorption of d-limonene (Arora and others 1991).

Commercial scalping-resistant packaging options. Some commercial packaging materials are specifically designed to circumvent the problems usually associated with flavor scalping.

For juices. International Paper Co. (Memphis, Tenn., U.S.A.) has introduced a new generation of “Super-Barrier™” Beverage packaging for juice and milk products, which helps lock in vitamins and retain flavor longer. International Paper’s patented Barrier-Pak (R) technology reduces flavor oil scalping by up to 20%, preserving the fresh taste of juice products.

The Lisle, Ill., based EVAL Co. of America recommends the use of EVOH in direct contact with juices to reduce flavor/ama ria migration (available from: www.foodproductdesign.com). EVOH provides an effective barrier even in the presence of moisture as flavor molecules are significantly larger than oxygen molecules. EVOH is not considered a recyclable material; however, 0.001 inches of EVOH provides the same barrier protection as 4.5 inches of HDPE (available from: www.foodproductdesign.com). It is advocated to use either PE/paperboard/PE/tie layer/EVOH/tie layer/PE/tie layer/EVOH in direct contact with the juice or a slightly simpler structure consisting of PE/PP/tie layer/EVOH. The barrier is an excellent way to protect juice from losing flavor and aroma compounds. Also, a relatively simple structure of HDPE/tie layer/EVOH/tie layer/EVA protects against flavor migration.

McLean Marketing has announced a new concept in packaging for Uncle Matt’s organic juices. The company is offering its organic orange juice in PET bottles that are claimed to offer many advantages, which for consumers could translate into better juice quality and taste plus an “easy to recycle” container. The PET packaging produces better juice quality over the life of the product, providing a better oxygen barrier with less flavor scalping.

Polymer nanocomposites have been demonstrated to help achieve packaged food a shelf life of 3 to 5 yr (Perchonok 2003). Aegis™ OX polymerized nanocomposite, oxygen-scavenging barrier nylon resin, specially formulated for high oxygen and carbon dioxide barrier performance, even in high humidity, is commercially available for a host of co-injection molded PET bottle applications, including bottles and orange juice containers. Another grade, Aegis™ NC, can be used as a coating or as the base resin for cast or blown films and replace nylon 6 coatings in paperboard juice cartons. The new family of resins nearly doubles the heat resistance of nylon 6 and has a potential for less flavor scalping.

For wines and liquor. A clear, high-barrier film that creates a superior oxygen barrier to protect wine packaged in bag-in-box wine casks is now available from Scholle Corporation (Chicago, Ill., U.S.A.), a supplier of wine bags worldwide (available from: www.bagnbox.com). This film replaces the traditional metalized PET film that used to be standard in the wine industry. It essentially doubles the shelf life of the wine, resists puncturing and flex-cracking, and can withstand the rigorous transportation conditions required for export. DuraShield is now being used in wine-producing countries worldwide. Using the latest polymer technology, it reduces flavor scalping. However, Flextank, a world leader in using PE for wine aging, maintains that food-grade PE of any density will retain its porosity in the presence of wine for many years resisting clogging by wine components or scalping flavor from the wine.

Cleartuf Power Polyester Resin (M&G Polymers USA, LLC, Tortona, Italy) is a PE terephthalate copolymer resin designed for liquor packaging and custom-packaging applications. It is a high-molecular-weight polymer designed to provide highly desirable container properties for the one-way packaging of tunnel-pasteurized beers (available from: www.mgpolymer.com). These include high clarity and sparkle, increased temperature and pressure stability, reduced flavor scalping, reduced carbon dioxide loss due to creep, and reduced carbon dioxide and oxygen permeability. Cleartuf Power Polyester Resin is designed with a special
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