

# Flavor Changes in Plastic Containers: A Literature Review

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Plastic packaging is an economical, attractive packaging option. However, it interacts with some ingredients in flavors and foods. This well-known drawback has been of major concern, as is evidenced by research dealing with the subject. Researchers in this field can tackle only a small part of the puzzle, however, due to a variety of factors that are difficult to control:

- Various types of plastic packaging are commercially available.
- An enormous variety exists in the components of the foods and flavors to be tested.
- Storage conditions differ.

This review looks at seven plastics commonly used in food containers (Table I). This number would be considerably higher if the various types of each plastic were considered. Accordingly, I do not concern myself here with factors such as the plastic's crystalline and polymer structure, or its porosity.

## Studies of Experimental Designs

The researcher needs to duplicate, as closely as possible, the packaging conditions that promote flavor changes. The setup design must consider the following interactions:

- Adsorption and/or absorption of flavor volatiles in packaging materials.
- Permeation of flavor volatiles through the plastic materials (loss to the atmosphere).
- Food- or flavor-induced changes in the physical properties of the plastic polymer rendering it, for example, more permeable to oxygen.
- Interactions of low-molecular-weight compounds in the plastic (such as solvent residues and plastifiers) with the flavor or food.

In reviewing the literature, I found that some experimental designs do not duplicate packaging conditions. As an example, some investigators<sup>1,3,5-7,9,10,14</sup> immersed the polymer materials in an aqueous solution of the flavor tested. Other researchers<sup>2,15</sup> mounted plastic pieces in the headspace of pure substances, such as limonene, through

**Table I. Plastic materials commonly used as food containers**

LDPE	Low density polyethylene, used mainly as inner sealing layer in multilayer packages, such as drink boxes from Combibloc Inc. (Columbus, Ohio) and Tetra Pak GmbH (Stuttgart, Germany)
MDPE	Medium density polyethylene
HDPE	High density polyethylene
PP	Polypropylene
PET	Polyethylene terephthalate, widely used for beverage bottles
PA	Polyamide
Suriyn	An ionomer resin used as the tie-layer between LDPE and aluminum sheet

which nitrogen was bubbling. Such a design ignored the important factor of partition coefficient between the food phase and packaging materials. A better setup is to pack the model solution in the same type of containers that will be used commercially. This approach is a better approximation of the real situation.

## Studies of Methods for Analyzing Flavor Changes

To investigate volatile changes, one approach is to measure the quantity of adsorbed and/or absorbed volatile in the container's material. Volatiles are then extracted from the plastic with solvents,<sup>4-6,13,19</sup> with supercritical carbon dioxide,<sup>1,14</sup> or through the application of thermal desorption processes.<sup>2,16</sup> The desorption process can cause inaccuracies, either because some of the volatiles do not get desorbed, or because some of the low-molecular weight compound residues in the plastic may get desorbed. Added to these inaccuracies are the inherent problems associated with the solvent concentration, usually required before GC injection.

In view of these difficulties, some researchers have measured changes in the volatile concentration in the model solution itself.<sup>3,7,8,10-12</sup> While this method eliminates the problems associated with desorption, it does not differentiate between a decrease of a volatile due to sorption and a decrease due to degradation within the solution. However, this drawback can be corrected by using a control of the same flavor or food, packaged in glass containers.

The author credits the following trade names and owners:  
TetraBrik is a trade name of Tetra Pak GmbH, Stuttgart, Germany  
Tween-80 is a trade name of Atlas Chemicals, USA  
Kool-Aid is a trade name of General Foods, USA  
FANTA is a trade name of Coca-Cola Company, Atlanta, Georgia

# Studies on Flavor Interactions with LDPE

Most studies were done with LDPE, which is extensively used in food and beverage packaging. The published results are difficult to compare because the authors used different experimental setup and assay methods:

- Apple flavor compounds in aqueous solution<sup>1,14</sup> and in apple juice.<sup>3</sup>
- Orange flavor compounds in orange juice.<sup>4,5,11,12</sup>
- Aqueous solutions of the selected volatile.<sup>7,9,19</sup>
- Commercial flavored yogurt drink.<sup>17</sup>

While some researchers measured partition coefficients, others measured sorption. Of the latter, some tried to determine volatile concentrations in the plastic, others measured the volatile remaining in the solution. At least the storage temperature during the sorption studies was the same in almost all publications: 20–25°C, with one exception<sup>4</sup> at 4°C. The volatile concentrations in all experiments were in the ppm region as in commercial flavored products. Important differences were in the ratios of plastic mass to solution volume ranging from 3 g LDPE per liter (this represents the conditions in a 1-liter TetraBrik package) up to 20 g per liter.

Despite these differences, I attempted to summarize the various findings. From Table II it can be concluded that hydrocarbons have the strongest tendency to migrate into LDPE, which is not surprising since polyethylene is apolar. The polarity of alcohols results in a quite low sorption. Aldehydes generally show a low affinity to LDPE, but with increasing C-chain length the polarity decreases and consequently the sorption increases. The sorption behavior of esters also suggests an influence of the C-chain length.

In a homologous series of saturated aldehydes (hexanal through dodecanal), the partition coefficient (plastic/solution) increased with the molecular weight<sup>19</sup> indicating an increase in sorption.

## Studies on Sorption Factors

**Time for establishing sorption equilibrium:** Equilibrium of the individual volatile between the solution and LDPE was reached within two to three days, according to some authors. Other authors report seven to ten days. This discrepancy may be due to different experimental conditions. Nevertheless, it can be concluded that sorption studies over more than two weeks are not relevant. After that time, the results may be influenced by chemical reactions such as browning reactions and vitamin C degradation occurring in juices.

**Influence of volatile concentration and presence of other volatiles:** Partition studies published by Nielsen et al.<sup>1</sup> showed that the partition coefficient of a volatile was constant over a wide range of volatile concentrations: the same percentage of volatile is absorbed by LDPE at all concentrations.

**Table II. Sorption (volatile loss) of selected substances packaged in LDPE (summarized by the author from published reports)**

Substance	Sorption (volatile loss)*			
	<10%	10-20%	20-35%	≥50%
<b>Hydrocarbons</b>				
limonene				•
myrcene				•
la-pinene				•
caryophyllene			•	
<b>Alcohols</b>				
butanol	•			
isoamyl alcohol	•			
hexanol	•			
trans-2-hexenol	•			
linalool	•			
<b>Aldehydes</b>				
hexenal	•			
trans-2-hexenal	•			
heptanal	•			
octanal	•			
nonanal		•		
decanal		•		
undecanal		•		
dodecanal		•		
geranial/neral	•			
perilla aldehyde	•			
benzaldehyde	•			
<b>Esters</b>				
ethyl butyrate C-6	•			
butyl acetate C-6	•			
butyl propionate C-7		•		
isoamyl acetate C-7		•		
ethyl 2-methyl butyrate C-7				•
hexyl acetate C-8				•
octyl acetate C-10				•

\* no results were reported in the 35-50% range

It was also found that some volatiles exhibit a lower sorption rate in mixtures with other volatiles than when they are alone in the solution. However, the difference was small, and there seemed to be no clear pattern to the different volatile categories.<sup>1,10</sup>

**Effect of pH:** Sorption of volatiles in aqueous solutions was found to be the same at pH 6 and 3.<sup>1</sup>

**Influence of storage temperature:** Table III shows Nielsen's measurements of the sorption of limonene and myrcene from commercial FANTA orange drink stored 12 weeks in PET bottles.<sup>13</sup> Possible reasons for increased sorption at higher temperature are:

- Increased mobility of molecules.

**Table III. Effect of storage temperature on quantities of selected volatiles absorbed from commercial orange drink stored 12 weeks in PET bottles**

Substance	Micrograms of absorbed volatiles per gram of PET material	
	at 4°C	at 25°C
limonene	3.40	9.90
myrcene	0.11	0.33

- Change in plastic configuration.
- Change in the volatile solubility in the aqueous phase.

**Influence of plastic surface and mass:** Researchers at Cornell University<sup>7</sup> investigated limonene sorption into LDPE by means of increasing the number of LDPE strips immersed into the aqueous solution. They found that the bigger the available plastic surface, the faster equilibrium is reached. With a low LDPE content it took up to 72 hours, but with ten times as many strips equilibrium was established in 12 hours.

Studies done at Tetra Pak GmbH<sup>4</sup> showed increasing limonene sorption with increasing thickness of the LDPE layer in contact with the solution.

**Table IV. Effect of plastic polymer on sorption rates of selected volatiles from orange juice**

Substance	Concentration of volatile at end of experiment Concentration of volatile at start of experiment x 100			
	LDPE (%)	HDPE (%)	PP (%)	Surlyn (%)
limonene	68	30	28	53
la-pinene	58	21	20	49
myrcene	66	28	22	78
caryophyllene	34	4	9	19
linalool	3	<1	1	2
octyl acetate	35	nd	13	21
decanal	18	6	6	11
undecanal	30	nd	12	14
dodecanal	22	7	9	16

nd = not determined

Shimoda et al.<sup>19</sup> confirmed these findings in sorption studies of octanal and nonanal solutions in contact with MDPE layers ranging from 30 to 70 microns in thickness.

### Studies Using Sensory Tests

Only a few authors have conducted sensory tests to go along with the analytical results. Kwapong and Hotchkiss<sup>7</sup> tested aqueous solutions of citrus oils, citral and benzaldehyde into which LDPE strips were immersed. Equilibrium was reached within three days, according to a GC assay of the solution. In a simple triangle sniffing test, the panelists could detect a difference in the odor above the samples containing orange, lemon and lime oil, but not in those containing citral or benzaldehyde. The relevance for the quality of the flavor profile was not checked.

Moshonas and Shaw<sup>11</sup> found that an aged/stale flavor developed in aseptically packed orange juice after storage for two weeks at 21°C or one week at 26°C, when compared to a control juice stored at 0°C. This off-flavor increased on prolonged storage. The authors attribute it mainly to an increase in the concentration of  $\alpha$ -terpineol, which, under acidic conditions, is probably formed from limonene by hydration.

Mannheim et al.<sup>8</sup> stored orange and grapefruit juices aseptically packed in LDPE-laminated containers and compared them to controls that were aseptically packed in glass jars. A triangle test revealed a difference in taste only after ten weeks of storage at 25°C. This was accompanied by a loss of vitamin C and an increase in brown color. Limonene decreased by 40%; other volatiles were not assayed. Since sorption equilibrium is reached after a few days, the change in taste can be attributed to other factors. The same authors did an additional test of LDPE strips in water for 48 hours at 35°C, after which a panel test identified an off-taste versus the control. Obviously, substances from LDPE had migrated into the water.

The research group at Tetra Pak<sup>4</sup> described a similar

**Table V. Effect of a PP plastic's density on sorption rates for limonene and l-carvone in aqueous solutions (emulsified with Tween-80)**

Density g/cm <sup>3</sup>	Sorption	
	Limonene (%)	l-carvone (%)
0.8830	75	17
0.9139	68	15
0.9213	63	10

**Table VI. Effect of plastic polymers on partition coefficients (K) of selected esters in aqueous solutions**

Substance	K			
	LDPE	PP	PA	PET
ethyl butyrate	2	4	0.5	0.5
butyl acetate	2	0.5	0.5	0.5
isoamyl acetate	5	9	0.5	0.5
ethyl 2-methyl butyrate	6	11	0.5	0.5
butyl propionate	7	19	1	1
hexyl acetate	25	45	2	4

**Table VII. Effect of polymer on partition coefficient (K) of selected volatiles in aqueous solutions**

Substance	K		
	LDPE	Surlyn 1652	Surlyn 1702
benzaldehyde	2	5	6
neral	15	23	14
geranial	22	40	24
limonene	4,800	4,400	2,800
ethyl butyrate	6	6	4

**Table VIII. Effect of polymer on sorption of selected volatiles from a commercial orange-flavored beverage powder**

Substance	Sorption units (mathematically derived)		
	LDPE	PET	Surlyn 1702
ethyl butyrate	80	10	90
myrcene	600	10	600
limonene	20,000	<1,000	35,000

study with orange juice in LDPE-laminated, gable-top packages, versus controls in glass bottles. The samples were stored at 4°C for up to 23 weeks. Although limonene losses of up to 50%, and small losses (~10%) of hexanal, trans-2-hexenal, octanal, nonanal and decanal were recorded, the flavor panel scores showed no significant difference. The reason could be the low storage temperature.

In 1985, Givaudan-Roure Corporation<sup>18</sup> conducted a trial with an orange-flavored drink containing 10% juice. The drink was aseptically packed in materials from Combibloc Inc. The researchers found increased concentrations of furfural as storage time increased. A cooked off-note was noticed after six months at room temperature; it became stronger after an additional three months of storage. No sorption studies were conducted.

### Studies with Different Plastic Materials

LDPE studies have shown that the sorption behavior of the different classes of volatiles depends to a great extent on their polarity. Different plastic materials have different polarities, hence their affinities toward volatiles may differ from LDPE.

Charara et al.<sup>5</sup> studied sorption rates from orange juice

containing beads of different polymers. Table IV shows the sorption percent of each volatile compared to its concentration in the juice at the start of the experiment. HDPE and PP have higher crystalline structures than LDPE, which explains the lower sorption rates.

Amorphous regions in the polymers have more affinity for volatiles. This was confirmed by Letinski and Halek<sup>10</sup> who determined sorption rates for limonene and l-carvone in aqueous solutions (emulsified with Tween-80) containing PP film pieces of three different densities (Table V). Their data demonstrated that the lower density polypropylenes, which have more amorphous regions, exhibit stronger sorption.

Partition coefficients (K) (see sidebar) of a series of esters in aqueous solutions containing pieces of plastic films were measured by Nielsen et al.<sup>14</sup> Their results (Table VI) contrast to some extent with the above findings. As the table shows, PP consistently displayed the highest partition coefficient of the four polymers assayed; hence, the highest sorption power. However, even with the highest partition coefficient, less than 10% of the volatiles in the solution were "lost" into the plastic phase. Larger ester molecules are less polar than the smaller ones and this

**Table IX. Effect of repeated washings on amounts of limonene and myrcene desorbed from PET bottles that had stored FANTA orange soft drink for 12 weeks**

Substance	Desorbed amounts (microgram per gram PET)			
	Just rinsed with water	NaOH wash		
		first time	second time	third time
limonene	4.5	3.7	3.7	3.1
myrcene	0.13	0.11	0.10	0.09

results in an increased affinity to the polymers.

A comparative study at Cornell University<sup>7</sup> with three different polymer discs immersed in aqueous solutions of volatiles reports the partition coefficients shown in Table VII. Surlyn 1652 has a higher affinity for the two citral components than the other two polymers. In all three plastic materials, limonene was sorbed to a much greater extent than the other volatiles.

Most studies were conducted with beverage models. But one report<sup>16</sup> deals with a commercial orange-flavored beverage powder (Kool-Aid) stored at 25°C in a sealed glass container with different polymer films mounted in the headspace. Here, the sorption is not determined by the partition coefficient between polymer and water phase, but by polymer/headspace/solid phase. The experimental

setup avoided direct contact between beverage powder and plastic material, which deviates from the conditions in "real life." Equilibrium was reached within 5-10 days. The figures in Table VIII are mathematically defined sorption units; high figures represent strong sorption. As in the trials with liquid beverage models, PET has a lower sorption affinity than LDPE and Surlyn, and ethyl butyrate shows less affinity for the apolar polymers than the hydrocarbon volatiles.

### Refillable PET Bottles

PET bottles for soft drinks are often recycled. After machine washing with 1.5% NaOH for 15 minutes at 60°C, they are refilled with fresh soft drink. Nielsen<sup>13</sup> studied the efficiency of washing in removing limonene and myrcene from the bottle material. FANTA orange soft drink was stored up to 12 weeks at 25°C in PET bottles. Volatiles were desorbed from the washed PET bottles by supercritical carbon dioxide extraction directly coupled to a gas chromatograph.

After repeated washing (manual lab procedure), Nielsen measured the amounts of volatiles in the PET material. Table IX shows that a large portion of limonene and myrcene remains in the bottle, even after extensive washing. This was further confirmed by the smell of the washed bottles after they were dried. The authors assume that machine washing in the soft-drink plants is more effective due to mechanical agitation.

As long as the bottles are refilled with beverages of the same flavor type, the sensory consequences are negligible.

### Conclusions

There is no plastic material completely without sorption capacity for flavor constituents. Sorption rate is related to differences in polymer characteristics and to the polarity of the different volatiles.

The majority of flavor components are more or less apolar; hence, from a flavor point of view, PET (polar) is preferable to polyethylene (apolar) as packaging material.

The degree of sorption is directly related to the available surface and mass of the packaging that is in contact with the food product.

Sorption reaches an equilibrium in less than two weeks of storage. Flavor changes occurring later can be attributed to other reactions taking place within the food matrix.

At higher storage temperatures, volatile sorption from beverages increases. At the same time, reactions within the beverages occur, and these reactions may affect the taste.

pH has no significant influence on sorption behavior.

The total loss of most volatiles important for the taste and flavor of a given food product can be estimated across the board at around 20% or less. Hydrocarbons in contact with LDPE can decrease more than 50%.

From all the published data, there is ample evidence that flavor constituents migrate from beverages and foods into plastic packaging materials. However, indications about

how relevant these losses are for the sensory profile of the product are insufficient, and should be emphasized in such work in the future.

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