Migration of Styrene in Relation to Food-Packaging Materials

– Review –

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Abstract

Polystyrene is frequently used for food packaging because of its easy processing, rigidity, and low cost. Styrene, which is present in detectable amounts in the polymer, is usually considered to be the substance responsible for the possible tainting of a polystyrene-packed food by migration. The contamination of foods and beverages by trace amounts of materials which have migrated from plastics used in packaging is a concern both on the grounds of adversely affecting product quality and of food safety. These lead to increasing attention to the potential hazards of a large variety of plastic materials which are used in the food packaging industry and the interaction between plastic packaging materials and foods. In this paper we reviewed the history of styrene and various analytical methods of sample preparation and detection to assess the extent to which styrene is present in food-grade polystyrene materials and to what extent it leaked into foods and food stimulants.

Key words: migration, styrene, food packaging, review

INTRODUCTION

The quality of a food product depends in some degree on the quality and nature of its packaging materials. A variety of packaging technologies are being developed to provide consumers with high quality, minimally processed foods that have a long shelf life. Food packaging has been dominated in the last few decades by innovations in plastic packages. These materials may be extruded into films, blow-molded into bottles, or layered onto each other for increased resistance to light, air, moisture, heat, puncturing and tearing. These include the development of different types of polymers, copolymers, the laminates, and packaging materials suitable especially for microwave heating.

Common flexible package materials are regenerated cellulose (cellophane), cellulose acetate, ethylene vinyl acetate (EVA), polyamide (Nylon-6), polyester, polyethylene terephthalate (PET), polystyrene, polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), and acrylonitrile (AN) (1). It is extremely difficult to obtain information on which plastics are used with what foods. For flexible films, the situation is further complicated because they are used in combination with one another, for example as coatings, as co-polymers and as laminates where complex systems are frequently necessary to achieve desired physical properties for specific applications (2). In addition to retail food packaging one should also be aware of the potential for contamination of foods arising from contact with plastics during food processing (e.g., plastic piping, processing equipment), during bulk storage and at the other extreme, from contact with plastics in the consumer home during food preparation in the kitchen (3).

The detection in beverages of vinyl chloride in 1974, associated with earlier findings on its carcinogenicity, has tended to center attention on the migration of monomers (3,4). These lead to an increasing attention to the potential hazards of a large variety of other plastic materials which are used in the food packaging industry and the interaction between plastic packaging materials and foods.

Rigid polystyrene (PS) and polystyrene-related plastics which are used as food-packaging materials have had a longer history of use than polyvinylchloride (PVC). Some of the physical characteristics of PS, for example, its low impact strength, easy processing, good transparency, rigidity, and chemical resistance, have led to the development of other food-use plastics in which styrene is copolymerised with monomers like butadiene and acrylonitrile, to give a flexible rubbery solid (1).

In this paper we reviewed the history of styrene and various analytical methods of sample preparation and detection to assess the extent to which styrene is present in food-grade PS materials and to what extent it leaked into foods and food stimulants. One of the practical concerns related to polymer packaging is not the presence of compounds in toxicologically insignificant amounts, but at levels affecting aroma and/or taste of the packaged food.

HISTORY OF STYRENE

Styrene ($C_6H_5CH=CH_2$) was first discovered in 1827 *via* the pyrolytic decarboxylation of organic acids of Storax balsam. Storax (styrax) is a pathological exudate produced in sapwood (balsam) and bark tissues of the trees *Liquidambar orientalis* and *Liquidambar styraciflua* (5).

Since that time, styrene has been identified as a natural constituent in a wide variety of foods and beverages. Styrene can be formed by bacteria in mold-ripened cheese, during the

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storage of grain (6,7), or during the fermentation of grapes. It is also possible that styrene can be formed during the biodegradation of structurally similar flavoring molecules (e.g., cinnamic acid, cinnamic aldehyde, cinnamyl acetate, cinnamyl alcohol, cinnamyl benzoate, and cinnamyl cinnamate) which occur naturally (8).

The French scientist Pierre Berthelot discovered a method for making styrene synthetically early in the 19th century. It was after World War II that styrene has used in the manufacture of numerous types of plastics. Approximately two-thirds of styrene monomer production is used in the manufacture of polystyrene (8).

Styrene is used in the production of plastics and resins such as polystyrene resins, acrylonitrile-butadiene-styrene polymer resins, styrene-acrylonitrile resins, styrene-butadiene copolymer resins, styrene-butadiene rubber, and unsaturated polyester resins. Examples are formed trays for meat or crystal clear trays for candy and cookies (Table 1). Polystyrene contains detectable amounts of residual styrene monomer which may be released into food and can be a potential source of off-flavor in the food product.

Styrene is efficiently metabolized to styrene oxide, which is itself readily detoxified by the same enzymes as those involved in the metabolism of various foodstuffs. Styrene oxide, like many intermediate metabolites of foodstuffs, is genotoxic and, if introduced directly into the stomach of rodents in high doses/concentrations, gives rise to cancers of the forestomach. Occupational exposure to styrene does not increase the risk of cancer generally or of cancers of the respiratory, digestive, or blood-forming tissues in particular. There is absolutely no basis for concern that nonoccupational exposure to styrene, which often occur as a consequence of migration from food-wrapping materials or through contact with styrene-based polymers, might increase the risk of developing any form of cancer. Tests for reproductivity have given negative results, but effects on blood dopamine and hypothalamic and pituitary function and menstrual cycling under conditions of very high exposure have been reported. In light of all the available information, it was concluded that migration of styrene from food-wrapping materials was not a matter for toxicological concern (4,9,10). Although the styrene monomer has been established as safe, its metabolism involves phenyloxirane, a mutagenic compound. Styrene is also considered to be the probable substance responsible for the tainting of a polystyrene-packed food by migration. Contaminated foods maybe (and in fact are) rejected by consumers due to off-tastes: it is well known that styrene has a very strong and repellent smell, and can be tasted in sour cream at a level as low as 5 ppb (11).

Polymers based on the styrene monomer can be produced with a wide range of properties by co-polymerization and the incorporation of rubber impact improvers (1,12). General purpose polystyrene (GPPS) gained early acceptance in the packaging field because of its easy processing, good transparency and rigidity, but these properties are offset by its poor impact strength, the ease of stress cracking and other characteristics such as the tainting of food by residual traces of monomeric styrene (1). The improvement in impact strength of more than 4 times by inclusion of synthetic rubber into the polymerization stage of manufacture led to the development of high impact polystyrene (HIPS). The important differences between general purpose and high impact grades are not only relative impact strength but also much higher ductility which is indicated by elongation at break. For food packaging applications, the permeability to moisture and atmospheric gases is also important.

Styrene, which is present in detectable amounts in the polymer, is usually considered to be the substance responsible for the tainting of a polystyrene-packed food by migration. Styrene can arise because of incomplete polymerization, followed by only partial removal during the devolatilization process and because of a breakdown of the polymer during processing. The level of monomer in commercial grades of polymer has been gradually reduced over recent years and is now generally guaranteed at less than 0.1% with a working level of about 0.05% (1).

MIGRATION

Migration is the term used to describe any mass transfer from the surface of the packaging to the food by physical and chemical action. The compounds which migrate (migrants) from plastic materials are usually residual polymerization residues (monomers, oligomers, catalysts, etc.) and polymer additives (antioxidants, plasticizers, heat/light stabilizers, antistatic agents, etc.). The extent of migration for a given migrant from a given polymer under defined storage conditions depends essentially upon the partition coefficient (K) which defines the ratio of the equilibrium concentration of the migrant in the polymer to that in the food. The partition coefficient, in turn, is a function of the composition of the foodstuff and

Table 1. Examples of polystyrene packaging and foods packaged

Form	Examples of food applications
Cups	Hot drinks
	Dairy products (yogurt, cream, cottage cheese)
	Honey
	Chocolate spread
Trays	
Formed	Fresh meat
	Fish
	Fruit
	Take-out food
Crystal clear	Candies
	Cookies
ABS[1] tubs	Margarines
Cutlery	Rigid polystyrene fork
Thermoset polyester	For microwave

[1]ABS (acrylonitrile-butadiene-styrene copolymer)

depends mainly upon its fat content (13).

In some food packaging, where there is no direct contact of the food surface with the polymer, vapor-phase migration of residual monomers and additives into food is thought to be a significant mode of transfer. This mode of transfer has been proposed for the migration of packaging components to dry foods (14) and has been shown to be possible for styrene migration from polystyrene (15).

For vapor-phase migration to occur, the styrene must first diffuse from the polystyrene-packaging material into the air space surrounding the food and then migrate from the air space into the food. Studies of the migration of styrene from GPPS and HIPS into air with subsequent absorption of the monomer into cooking oil, "vapour-phase" migration, was determined in a sealed system (16). The result showed that for both polymers the amount of styrene migrating from the polystyrene and being absorbed by the oil was proportional to the square root of the time of exposure. The diffusion co-efficients that were calculated for the vapor-phase migration of styrene from GPPS and HIPS were found to be in good agreement with the diffusion coefficients determined for the liquid-phase migration of styrene from similar polymers where the polymers were completely submerged in cooking oil at or below 150°F (12), and indicated that vapor-phase migration is equivalent to liquid-phase migration for temperatures studied below 180°F. It was also indicated that the styrene concentrations measured in both experiments (12,16) were due to the intrinsic diffusion of styrene from polystyrene, and that the external matrix had little or no effect on the diffusion of styrene from the polymer (below 180°F) (16).

EXPERIMENTAL MIGRATION STUDIES

Sampling

Experimental determination of styrene migration was conducted through several methods. The following steps were used in general: (1) contact the samples of the packaging material with a food or food-simulating liquid (FSL), (2) at regular intervals withdraw a sample of the FSL and determine the quantity of the substance that has migrated from the plastic, and (3) collect and analyze the data.

Several sampling methods have been developed for testing the amount of styrene monomer migration. Usually, migration studies are carried out using food-simulating agents, such as distilled water, vegetable oils or HB 307 (17,18), because it is impractical to use real food products in migration tests (19). Contact with the polymer can be established by cutting the material into pieces, immersing in a food-simulating agent and incubating the sample at a given temperature, usually 40°C (20,21) (Immersion sampling). Cutting the styrene polymer can disturb its physical structure, results in an overestimation of migration in food simulants (22). The United States Food and Drug Administration in cooperation with Arthur D. Little Inc. developed standard tests using sampling cells for carrying out migration experiments with liquid and solid foods

(17,23-26). The area of contact between liquid and polymer can be varied by the number of polymeric disks used (Cells for sampling). Giacin (27) describes migration as a two-step process: diffusion of migrant through the polymer bulk phase to the polymer surface and subsequent dissolution or evaporation of migrant present at the surface. It was suggested that transfer at the interface involves a vaporization step from the plastic package followed by absorption into the solid food (14). Vapor-phase migration could be carried out by cutting the polystyrene and attaching it to a thread fastened on a wire, which is clenched in an excavated Erlenmeyer stop (15,16).

Foods are complex systems which do not lend themselves readily to isolation and identification of trace components that have migrated from packaging materials at levels of ppb or below. Sensitive analytical techniques are required to measure residual monomers in the polymer matrix when present at the part-per-million level and below. Currently, volatiles are analyzed using either headspace or purge-and-trap methods. The main difficulty in their determination is their isolation from various matrices. The isolation of styrene from solid, fatty of aqueous matrices has been carried out. Methods for isolation of styrene from dairy products have involved solvent extraction (28), distillation (29,30), or azeotropic and vacuum distillation (31,32) and also by static and dynamic headspace methods.

Analysis

Headspace gas chromatographic analysis

Several authors have described headspace gas chromatographic methods for the determination of volatile components in polymeric materials (3,4,28,29,33-38). These techniques offer distinct advantages over direct-injection GC techniques. The most important advantages are prevention of column contamination, reduction of interference arising from the injection of large amounts of solvent, and enhanced sensitivity. Headspace gas chromatography consists, essentially, of placing the sample for analysis in a closed vessel, allowing the compound of interest to equilibrate between the sample and the surrounding vapor usually by heating in order to obtain rapid equilibration and finally to inject a sample of this equilibrated "headspace" into a gas chromatograph. At low concentrations the ratio of the concentration in gaseous phase to the concentration in aqueous phase is a constant (partition coefficient) and is unique for each organic compound. By analyzing the gaseous phase and applying the appropriate partition coefficient, one can calculate the concentration of each organic initially present in the aqueous phase.

It also offers a distinct advantage in that sample work-up procedures have been avoided. The latter usually involves distillation, extraction, and/or adsorption processes, and almost invariably engenders quantitative loss and, frequently lead to qualitative changes in the composition of the sample, which are certainly good reasons to favor simple headspace injections. Unfortunately, these simple headspace injections also suffer

a disadvantage: to obtain optimum chromatographic results, it is necessary that the injected sample occupies a minimum length of column as the chromatographic process begins. If this concept is violated, one pays the price in broad, poorly resolved peaks: hence the size of sample gas that can be injected is seriously limited.

Both the chemical composition and physical state of the sample matrix can affect the head space composition. The analysis of flavor in packaging materials generally involves head space gas chromatographic techniques. It is simple and reproducible; however, sensitivity of the analyses is too low. Although concentration of headspace onto polymers can increase the sensitivity, it requires the use of correction factors because individual volatile compounds have different affinities for the adsorbent.

Styrene is not an ideal candidate for analysis by headspace chromatography, for with a boiling point of 145°C its volatility is low in comparison with VC, VDC, or even AN. However, as the concentration of styrene in polymers is relatively high, the limit of detection of 1 mg/kg styrene can be achieved by a modified solution headspace approach (38). This modified technique involves dissolving the polymer in an organic solvent (N, N-dimethylacetamide) in the normal manner and then altering the composition of the solvent phase to decrease styrene solubility and thereby increase its equilibrium concentration in the headspace. For this purpose water was found to be the most effective solvent, since water is normally free of interfering organic contaminants and it will not be sensed by the GC/FID.

Purge and trap gas chromatographic analysis

Dynamic headspace/gas chromatography (DH/GC) has gained popularity as an effective and sensitive technique for the analysis of volatile compounds (8,39,40-42). The study of a dynamic system was initiated whereby a sweep (purge) gas is bubbled through the sample until the volatile organics are quantitatively transferred to the gaseous phase. The organics that are quantitatively transferred to the gaseous phase could then be concentrated for gas-chromatographic analysis with the use of a noncryogenic trapping technique for ambient-air and dilute-emission analysis. In this manner an analysis performed upon the gas phase would have a direct relationship to the aqueous-phase concentration (39).

This can be either on-line or off-line. In off-line GC, styrene is swept from the matrix by a purge gas such as helium or nitrogen and trapped in a solvent or an adsorbent, from which it is then eluted. In on-line GC, preconcentration can be carried out on an adsorbent, or on a cryogenic trap. The saturation by a gas (CO_2, He, or H_2) of saturated sodium chloride solution strongly enhanced desorption of the aromatic hydrocarbons from model media (40). The nature of the purge gas has little effect on purge efficiency: nitrogen, carbon dioxide and hydrogen gave similar recoveries (40). The best conditions for the desorption of the volatile aromatic hydrocarbons involve a short preliminary bubbling of carbon dioxide into a saturated NaCl solution, which is then added

to the sample just before starting the purge. When this method was applied to dairy products, use of CO_2 was disregarded since it induced extensive foaming of the dairy products in the cell. Helium was preferred to H_2 as carrier gas since it enabled better regulation of pressure.

It is necessary to use both conventional food simulants and standardized test conditions which are supposed to simulate the migration behavior of substances into foods under actual conditions of use. The EC (13) directive lists the following food simulants: (1) distilled water or water of equivalent quality; (2) 3% (w/v) acetic acid in aqueous solution; (3) 15% (v/v) ethanol in aqueous solution, and (4) rectified olive oil; if necessary, a synthetic triglyceride (e.g., HB 307) or sunflower oil may be used. For example, milk product, as widely consumed foodstuffs with fat contents ranging from 0 to 80% and commonly packed in polymeric materials, merited investigation with respect to possible migration. Milk products have been generally considered to be aqueous systems due to the fact that an aqueous solution of carbohydrate, protein and salts represents the continuous phase of milk surrounding fat globules and casein micelles. The EC directive prescribes the use of water or 3% acetic acid for migration testing of packaging materials for milk products, depending upon pH. Recent study of measurement (13) of styrene monomer migration from polystyrene cups into milk containing 0.5, 3.5 or 10% fat into four water/ethanol mixtures, containing 0, 15, 50 or 100% ethanol, indicated that pure water gave migration values considerably lower than all of the three milks. Only 50% ethanol was shown to correlate approximately with 3.5% fat milk. They concluded migration testing employing such aqueous food simulants will necessarily lead to underestimation of the migration processes occurring in real milk products

SENSORY EVALUATION

Sensory test results of single stimulus do not necessarily provide information for the understanding of the more complex stimuli which arise from mixtures. It has been found that, even for simple mixtures, components may interact to produce marked and unpredictable changes in the quality and intensity of the stimulus (43). A series of reports were proposed to characterize the threshold properties of the mixtures in one of the following four possible categories (44,45): (1) independency: no stimulus would be perceived unless at least one compound in the mixture was at or above its threshold concentration. (2) addition: a stimulus would first be perceived in a mixture where individual subthreshold fractional concentrations reached a total threshold of 1. (3) synergism: stimulus would first be perceived in a mixture of compounds each at less than its individual threshold concentration and the total of the fractional contributions was less than 1. (4) mask: no stimulus would be perceived in a mixture with each compound at its threshold concentration. A numerical taste unit formula was developed (45) to place mixtures into these

categories.

Recent studies focused on the effect of mixtures of styrene and ethylbenzene on detection threshold level (46). A 5% oil-in-water (O/W) emulsion was used as a food stimulant because styrene and ethylbenzene can be easily dissolved in the fat fraction. A detection threshold concentration of 1.0 ppm for styrene and 3.0 ppm for ethylbenzene was found in a 5% O/W emulsion using the constant stimulus differences test and mixing of styrene and ethylbenzene showed an additive effect at subthreshold levels. Finally, the results showed that composition of the mixture does not influence the mixing effect at subthreshold levels. Since both compounds are aromatic hydrocarbons with monosubstituted benzene rings, the results correspond with the findings of Guadagni et al. (44), i.e., compounds closely related in structure and functional groups exhibit additivity. However, opposite results were also found in the literature. Durst and Laperle (41) calculated that styrene/ethylbenzene mixtures showed a synergistic influence on off-flavor detection. In their study, a plastic-like off-flavor in food packaging in multilayered polystyrene containers was determined to be predominantly caused by a residual styrene monomer, in conjunction with ethylbenzene, that had diffused into the food product. When the styrene/ethylbenzene concentration was reduced to 25 μg/L, a significant flavor difference could be detected. In contrast, 50 μg/L styrene alone was necessary to be perceived by the panel at the 99% confidence level, and ethylbenzene could not be perceived at even 100 μg/L when added alone to the juice. This synergistic relationship between styrene monomer and ethylbenzene is important in correcting styrene-like flavor problems.

Partition coefficients and absolute flavor thresholds were determined in high-fat containing cookies for 11 organic compounds to study the partitioning behavior and absolute flavor thresholds of two series of compound by Halek and Levinson (47). They consisted of a homologous series of aliphatic esters and of aromatic hydrocarbons selected to determine if structural features or functional group similarities would elicit definite relationships. The two groups of structurally and functionally related compounds exhibited similar individual thresholds but the heterogeneous group gave widely different values. Mixtures of these compounds at subthreshold and threshold concentrations gave interactions that could be sorted into additivity or independency according to group similarities. Application of numerical categorization formulas did not show consistent correspondence with word definitions of additivity or independence.

In another case, chocolate and lemon cookies packed in polystyrene trays and overwrapped with cellophane developed an off-flavor due to migration of residual styrene monomer from the polystyrene trays (47). Analysis of the trays, however, showed residual monomer levels of 0.18~0.20%, well below the specification maximum of 0.5%. The package was thus acceptable according to compositional limits but resulted in the tainting of the food.

TYPICAL STYRENE LEVELS

It is obviously difficult to generalize about levels of monomers likely to be found in retail packaging and foods. Only very limited data are currently available for styrene levels. It is generally recognized that styrene levels in plastics are significantly higher than those found for the other monomers, partly because of polymer solubility in the monomer and facile depolymerization which occurs on heating of the polystyrene. The limited data available for retail foods however show that styrene levels are not proportionally higher than for other monomers, and example levels ranging from 0.005 to 0.04 mg/kg have been found in single cream (3).

Following the increased use of microwave ovens and combination ovens, there has been a corresponding requirement for cooking articles which can be used in both a microwave oven and a conventional oven, i.e., dual-ovenable. Plastics used in microwave cooking have shown an increase in migration with the higher temperatures experienced during the cooking (48). In conventional ovens, temperatures up to 210°C may cause even greater migration (49). The identification of volatile potential migrants including styrene from dual-ovenable plastics by dynamic headspace/gas chromatography/mass spectrometry was described by Gramshaw et al. (50).

Thermoset polyester is made by cross-linking chains of an unsaturated polyester with a third monomer, usually styrene. There is a high residual styrene content after curing in the mould, which is reduced by a period of heating (postcuring) for up to 15 min. The finished product is a hard, durable plastic with a ceramic-like feel. Thermoset polyester is used for dual-ovenable cookware designed for repeat home use, such as roasting racks, cake dishes and casserole dishes.

Static headspace analysis in conjunction with solvent extraction has been used to measure the levels of some volatiles in thermoset polyester. However, the solvent extraction/static headspace analysis cannot guarantee complete extraction and can only give a lower limit for the levels of volatiles in the plastic (51). The static headspace methods used were only suitable for compounds with a low boiling point. Migration of styrene into foods and olive oil was measured by a similar method with the addition of cyclohexane to the slurred food to improve headspace partition (37).

The levels of styrene in samples of thermoset polyester were determined by dynamic headspace/gas chromatography. Styrene was present at levels from 50 to 1400 mg/kg. Styrene was shown to be produced by thermal depolymerization at temperatures of 175°C and above. The migration of styrene into pork belly (bacon) cooked in thermoset polyester dishes for 1.5 h at 175°C was measured by Likens-Nickerson extraction of the cooked meat and GC/MS analysis of the extracts were in the range of 6 to 2400 μg/kg (52).

CONCLUSION

Despite the complexity of the topic of food packaging, substantial advances have been made over the past 15 years,

which offer benefits to the consumer. The visual and aesthetic image created by packaging is now a sales strategy of the same order as the quality of the food product itself. However, precautions have to be taken to avoid off flavor development during production as well as during packaging by sensitive and efficient quality control so that satisfactory products can be presented to consumers. Finding the causes and origins of the off-flavor is of importance, so that new and more suitable packaging materials may be selected. Developing a better understanding of the theoretical basis of migration as well as representative analytical methods will lead to the reduction of the level of trace contamination of foods from packaging materials.

In order to predict the potential exposure of consumers to styrene from food packaging applications, the correlation of residual styrene concentrations in polystyrene packaging with styrene migration into food simulating solvents or retail foods were examined using various sensitive analytical techniques.

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