DETERMINATION OF STYRENE MIGRATION FROM POLYSTYRENE CUPS INTO SOME FOODSTUFFS AND FOOD SIMULANTS

Gomaa, R.B.A.
Food Technol. Res. Inst., Agric. Res. Center, Giza, Egypt

ABSTRACT

The level of styrene migration from polystyrene cups was monitored in different food systems including: cold beverages (orange juice, apple juice, Coca-Cola, 7 up), hot beverages (tea, coffee, chocolate drink), water, milk (0.5, 1.5 and 3.5% fat), take away foods (jelly and ice-cream), as well as aqueous food simulants (3% acetic acid, decanol, 8, 20, 50 and 100% ethanol). Styrene migration was found to be strongly dependent upon the fat content, time and storage temperature. Water gave migration values considerably lower than all of the fatty foods. Ethanol 20% showed a migration level equivalent to milk of 3.5% fat. Food simulants were responsible for higher migration in case of 100% ethanol at 40°C for 24 h. However, at 70°C at 24 h, was observed that styrene levels of the decanol were much higher than those of the other simulants. Styrene migration rate into hot beverages was always higher than that obtained in case of cold beverages used in the present study.

INTRODUCTION

The diffusion of chemicals from polymers is of interest to the U.S. Food and Drug Administration (FDA) in its regulation of polymeric food packaging materials (Synder and Breder, 1985).

Styrene is one of the most widely used monomers in food contact polymers. Various types of polystyrene cups, including foam, impact and crystal were tested. The primary food contact applications of polystyrene are containers for yogurt, cream, cottage cheese, ice cream and fruit juice, meat trays, biscuit trays, egg cartons, take-away food and drink cups, and produce boxes (Flanjak and Sharrad, 1984).

In the united Kingdom, cups for vending machines and disposable drinking containers are estimated to account for some 45% of the total production of food-grade rigid polystyrene (Castle *et al.*, 1991).

Styrene can be concluded in high concentration in rigid polystyrene and is apparently difficult to remove from the finished products. In addition, the heat applied in processing, the polymer causes degradation and the formation of additional styrene. Thus, polystyrene food packaging would reasonably be suspected to contain styrene.

Styrene is vinyl-substituted benzene. Like vinyl chloride, it is believed to be metabolized in human via an expoxide intermediate (Ohtsuji and Masayuki, 1971). *In vitro* expoxide formation by liver microsomal enzymes has been demonstrated.

Residual monomers in food contact polymers are known to migrate into foods, and there is growing interest in the effects of some of these chemicals on human health. Several adverse health effects are attributed to styrene. Humans experience, eye, nose, throat, and skin irritations when exposed to the vapours. Styrene has a toxic effect on the liver, acts as a depressant on the control nervous system, and causes neurological impairment. An increase in the frequency of chromosomal operation has been observed in the lymphocytes of human subjects occupationally exposed to styrene (Varner *et al.*, 1983).

Previous work indicated that styrene levels of 60-2250 ppm were present in polystyrene food packaging (Varner and Breder, 1981). Withey and Collins (1978) reported that styrene detected in dairy products at levels up to 245 ppb in sour cream. In hot chocolate and chocolate spread, they contained 13 ppb and 2 ppb, respectively.

Gilbert and Startin (1983) found different levels of styrene in food products, e.g. 180 ppb in chopped candied peel. Varner *et al.* (1983) examined the styrene migration into margarine and found that there was no detectable migration.

The monomer migrated into food simulating solvents from various styrene-containing beverage cups. In studies simulation filling and storage at room temperature, the average values for

styrene migration into 8 % ethanol, $\mu g/cm^2$ of container were 0.036 (27 ppb) for foam cups, 0.064 (52 ppb) for impact polystyrene containers, and 0.210 (151 ppb) for crystal polystyrene glasses. Using water, coffee and tea, an average of 0.0078 $\mu g/cm^2$ (6.3 ppb) styrene migrated from foam cups under conditions simulating hot filling or pasteurization above 65.6°C (Varner and Breder, 1981).

Snyder and Breder (1985) studied the migration of styrene from polystyrene into various solvents. They concluded that styrene migration at similar rates into 20% ethanol, corn oil, and HB-307 (a synthetic triglyceride).

This paper evaluates the levels of food contamination by styrene monomer derived from food contact materials, especially disposable drinking containers. Different parameters including the fat content, temperature and time were taken in consideration.

MATERIALS AND METHODS

Cups:

Clear polystyrene cups (volume 200 ml, surface area 1.30 dm^2), which are commonly used for cold and hot drinks were collected from the local market.

Samples:

Foodstuffs: Different foodstuffs involved in this study included:

1. Milk samples with different fat contents (0.5, 1.5, 3.5%).
2. Cold beverages (apple juice, orange juice, cola, 7up, distilled water).
3. Hot beverages (tea, coffee, chocolate drink) obtained as dry powders, and were reconstituted with boiling distilled water before use.
4. Jelly prepared before putting in cups, and
5. Ice-cream packed in cups before storage.

Samples were purchased from supermarkets, and stored at 4 $\pm$ 1°C until analysed. The samples were usually stored for no longer than seven days before analysis.

Food simulants:

Acetic acid 3%, and ethanol 8, 20, 50 and 100%.

Acetic acid with purity 99.5% was used for preparation of acetic acid water solution 3% by volume as well as ethyl alcohol 95% purity was used for preparation of ethanol-water solution 8, 20, 50 and 100% by volume.

HPLC:

Chromatographic analysis was performed with and Analyser HPLC (model 305) with UV/V1S absorbance detector and a data module integrator/recorder. The column (250 x 4.6 mm) was packed with Lichrosorb RP-18 10 µL and the mobile phase was distilled water-aceto-nitriale (25%-75%) at flow rate of 1.0 ml/min. Sample injection volume was 50 µL. The detector was set at 245 nm.

Determination of styrene in polystyrene cups:

A cup was weighted, cut into pieces, dissolved in dischloromethane, and subsequently precipitated with iso-octan. The sample was centrifuged at 4000 rpm for 20 min. The clear supernatant was removed and concentrated to about 1.0 ml for HPLC analysis as described above.

Test conditions:

The test conditions of the samples are shown in Tables (1 and 2) as given by Tawfik and Huyghebaet (1998).

Two replicates and two duplicate samples at timed intervals were performed for every experiment.

For testing of food simulants, (3% acetic acid, 15, 50 and 100% ethanol, the test conditions were 1 h at 100°C and 24 h at 40°C.

Table (1): Test conditions applied in migration experiments with hot and cold beverages.

Beverage	Time	Temperature (°C)
Distilled water	1 h	100
	2 h	100
	2 h	80
	3 days	60
	3 days	40
	3 days	20
	3 days	4
Orange juice	16 h	20
Apple juice	16 h	20
Cola	16 h	20
7up	16h	20
Jelly	1 day	4
	3 days	4
	7 days	4
Ice-cream	30 days	-10
	60 days	-10
Tea	1 h	100
Coffee	1 h	100
Chocolate	1 h	100

Table (2): Test conditions applied in migration experiment using milk with of different fat content.

Time (hour)	2	2	2	2	24	2	24	24	72
Temp. °C	100	80	60	40	40	20	20	4	4

RESULTS AND DISCUSSION

Migration studies of styrene from polystyrene (PS) cups into hot and cold beverages and food simulants:

Recovery of added styrene from various foods is presented in Table (3). The range of recovery was 79.4% to 96.2%, the lowest being in ice-cream and the highest value with water. The determined amount (mean of two determination from two cups) of styrene in polystyrene cups was 91.4 ppm.

Table (3): Recovery of added styrene from various foods.

Sample	Amount added mg/kg	% recovery
Juice	0.05	95.9
Water	0.05	96.2
Milk	0.05	93.7
Ice-Cream	0.05	79.4

Migration of styrene from polystyrene cups into hot and cold beverages comparing to distilled water:

The migrated levels of styrene monomer from the PS cups into water at different incubation temperature and time are presented in Table (4). The migration level increased with increasing storage time at constant temperature, and the rate was accelerated by increasing storage temperature. the migration of styrene to water at 100°C was 0.002 mg/dm^2 after one hour. However, after 2 hours of storage the concentration of styrene increased to 0.004 mg/dm^2 at the same storage temperature. The migration of styrene to water at 20 °C and 4 °C were 0.002 and 0.0002 mg/dm^2 after 3 days of storage, respectively. Durst and Laperie (1990) indicated that at a constant temperature, the styrene pic-up should be proportional to the square root of the time for some initial period.

The rate of migration into the tested products (jelly and ice-cream) were recorded in Table (4). It can be observed that the styrene concentration increased with increasing time at constant temperature. Whereas, the styrene migrated from PS cups into jelly were 0.0003, 0.0009 and 0.001 mg/dm^2 after 1, 3 and 7 days at 4°C, respectively. Also, it can be observed that the styrene migrated from PS cups into ice-cream increased with increasing storage time at constant temperature. They were 0.004 and 0.006 mg/dm^2 after 30 and 60 days at -10°C, respectively of contact in actual use.

In the case of cold beverages, the European community test conditions (EEC 1985) close to those of expected use were chosen (about 16 hour at room temperature), whilst exposing the vending machine cups to hot beverages for one hour at 100 °C is for more rigorous than any real exposure, as a beverage, does not come from a machine at this temperature, and anyway would cool very rapidly. Directive 93/8/EEC lays down the test conditions to be chosen

according to conditions. They found that the amount of styrene migrated per unit area was 0.001 mg/dm^2 for foam cups with water, tea and coffee.

Table (4) also indicated that the styrene migration from PS cups into orange juice, apple juice, coca cola and 7up were (0.0007, 0.0009, 0.0009 and 0.0008 mg/dm^2 after 16 h at 20°C, respectively. For hot beverages (tea, coffee, and chocolate), in all cases styrene migration occurred. The amount of styrene migrated was in the range of 0.002 mg/dm^2. Varner and Breder (1981) reported that hot coffee and tea extracted styrene at the same rate as did hot water.

Table (4): Migration of styrene from polystyrene cups into hot and cold beverages.

Beverage	Test conditions	Styrene residues* mg/dm^2
Distilled water	1 h at 100°C	0.002
	2 h at 100°C	0.004
	2 h at 80°C	0.002
	3 days at 60°C	0.0046
	3 days at 40°C	0.004
	3 days at 20°C	0.002
	3 days at 4°C	0.0002
Orange juice	16 h at 20°C	0.0007
Apple juice	16 h at 20°C	0.0009
Cola	16 h at 20°C	0.0009
7up	16 h at 20°C	0.0008
Jelly	1 day at 4°C	0.0003
	3 days at 4°C	0.0009
	7 days at 4°C	0.001
Ice-cream	30 days at -10°C	0.004
	60 days at -10°C	0.006
Tea	1 h at 100°C	0.002
Coffee	1 h at 100°C	0.002
Chocolate	1 h at 100°C	0.002

* Results presented as an average of two determination from two samples.

Migration of styrene from polystyrene cups into milk with different fact contents:

The results of migration of styrene from PS cups into milk with different fat content are recorded in Table (5). The migration of styrene from the cups into whole milk (3.5% fat) was more than

into half-fat milk (1.5% fat) and both were more than into skimmed milk (0.5% fat) at different temperatures and storage times. The differences between milk with various fat percentages were clearer at the highest temperatures (100, 80 and 60°C) after 2 hour of storage, but there were no significant differences between them at 40 and 20°C (Figure 1). These results are in agreement with the results of O'Neill *et al.* (1994) who measured the styrene migration from polystyrene cups into milk containing 0.5, 3.5 or 10% fat. They concluded that water gave migration values considerably lower than all of the three milk types. Ramshow (1984) stated that the amount of migration styrene was higher in products with a higher fat content.

Table (5): Migration of styrene from polystyrene cups into milk with different fat contents.

Beverage (sample) / Test conditions	Styrene residues (mg/dm^2)		
	Whole milk (3.5% fat)	hall-fat milk (1.5% fat)	Skimmed milk (0.5% fat)
2 h at 100°C	0.02	0.015	0.007
2 h at 80 °C	0.008	0.006	0.003
2 h at 60 °C	0.004	0.0009	0.0004
2 h °C 40 °C	0.0002	0.0002	0.0001
24 h at 40 °C	0.005	0.0003	0.002
2 h at 20 °C	0.0001	< 0.0001	< 0.0001
24 h at 20 °C	0.003	0.002	0.0009
24 h at 4 °C	0.0001	< 0.0001	< 0.0001
3 days at 4 °C	0.0007	0.0002	< 0.0001

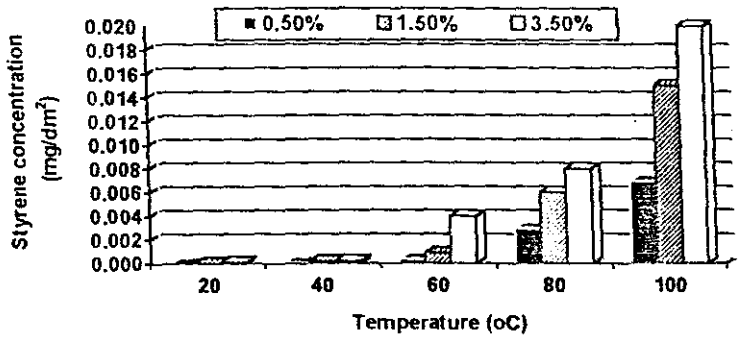

Fig. (1): Migration of styrene from polystyrene cups into milk of different fat contents after 2 hours of storage at different temperatures.

Migration of styrene from polystyrene cups into food simulants:

The migration of package ingredients directly into food products is often difficult to analyze instrumentally because of interference from food ingredients. Consequently, it is necessary to use both conventional food simulants and standardized test conditions which are meant to simulated the migration behaviour of substances into foods under actual conditions of use (O'Neill *et al.*, 1994). The directive 82/711/EEEC lists the following food simulants: (a) distilled water of equivalent quality; (b) 3% (w/v) acetic acid in aqueous solution; (c) 8, 20, 50% (v/v) ethanol in aqueous solution; and (d) decanol. Data obtained for the styrene migrated from PS cups into tested food simulating liquids are reported in Table (6). Consequently, Fig. (2) illustrates the comparison between the concentration of migrated styrene, in mg/dm^2 from PS cups into the tested food simulants liquids. In the current study 3% acetic acid, ethanol (20, 50, 100%) and decanol were used as food simulants. From the data illustrated in the above mentioned Table (6) and Fig. (2) it can be observed that the styrene migration relatively increased in order of 8% ethanol < 3% acetic acid < 20% ethanol < decanol < 50% ethanol < 100% ethanol after one hour at 100°C. The greatest styrene migration was observed with decanol as a food simulant followed by 100% ethanol then the other food simulant after 24 hours at 70°C. However, the lowest styrene migration was observed in the case of 3% acetic acid.

From the same reported data, the rate of styrene migration was decreased with decreasing storage temperature to 40°C after the same time (24 hours). Where, they were 0.009, 0.008, 0.005, 0.004, 0.003 and 0.002 mg/dm^2 for 100% ethanol, 50% ethanol, 20% ethanol, decanol, 8% ethanol and 3% acetic acid after 24 h at 40°C, respectively. Snyder and Breder (1985) studied the migration of styrene from PS cups into various solvents; water, 3% acetic acid, 8, 20, 50 and 100% ethanol, corn oil, heptane, hexadecane and decanol. They reported that all solvents extracted only 1-2% of the total available styrene with the exception of 100% ethanol, which extracted 7% after 2 weeks at 40°C. In addition, Jickells *et al.*

(1993) reported that testing for 2 h at 175°C into olive oil resulted in significantly high migration of styrene.

Fig. (3) illustrates the comparison between the styrene migration from PS cups into milk different fat contents and different concentration of ethanol in water after 24 hour at 40°C. The 20% ethanol was correlated approximately with 3.5% fat in milk. Whereas, highest differences were observed in the styrene migrated in cases 50, 100% ethanol and 0.5, 1.5, 3.5% fat. In a previous study by O'Neill *et al.* (1994) the styrene concentration found in the 3.5% fat milk was assumed to be comparable to that of the 50% ethanol.

Table (6): Migration of styrene from polystyrene cups into food simulants.

Food simulants	Test condition	Styrene residues mg/dm^2
3% acetic acid	1 h at 100°C	0.004
	24 h at 70°C	0.006
	24 h at 40 °C	0.002
8% ethanol	1 h at 100°C	0.003
	24 h at 70°C	0.009
	24 h at 40 °C	0.003
20% ethanol	1 h at 100°C	0.005
	24 h at 70°C	0.01
	24 h at 40 °C	0.005
50 ethanol	1 h at 100°C	0.02
	24 h at 70°C	0.03
	24 h at 40 °C	0.008
100% ethanol	1 h at 100°C	0.03
	24 h at 70°C	0.05
	24 h at 40 °C	0.009
Decanol	1 h at 100°C	0.008
	24 h at 70°C	0.06
	24 h at 40 °C	0.004

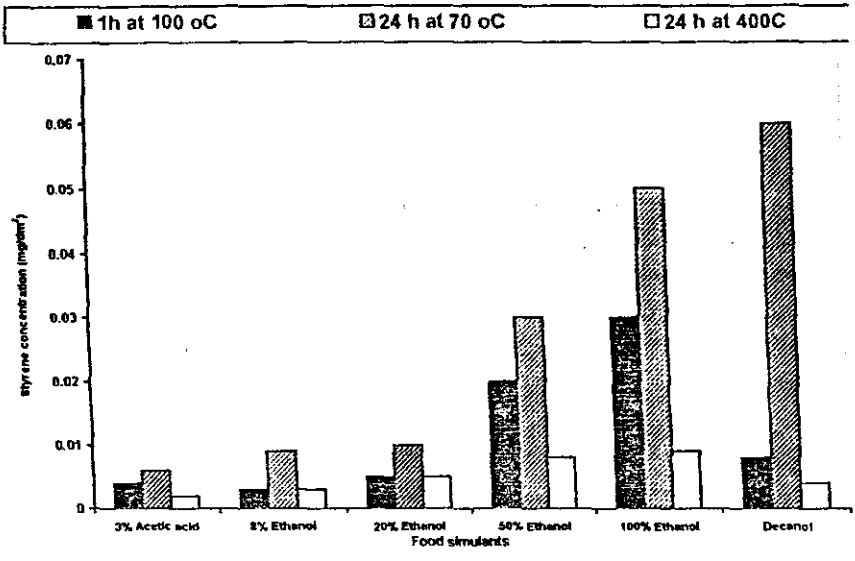

Fig. (2): Concentration of styrene migrated with time into food simulating liquids stored at different temperatures.

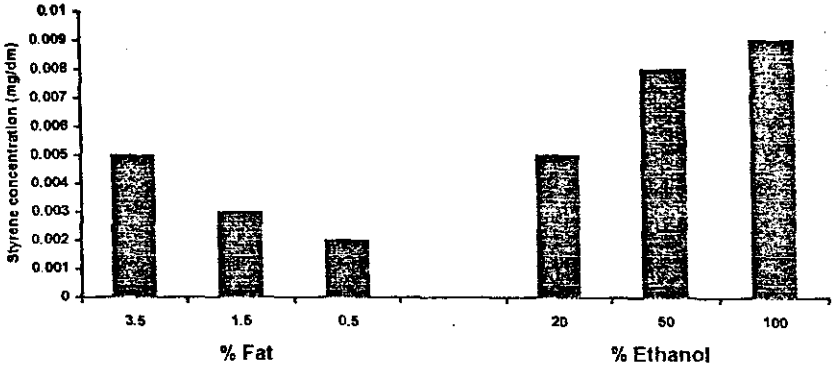

Figure (3): Migration of styrene from polystyrene cups into milk of different fat content after 24 hours at 40°C compared with different concentrations of ethanol in water.

CONCLUSION

From the obtained results it could be concluded that:

The level of migration essentially depends upon the fat content, storage temperature, and time. Migration testing employing aqueous food simulants will necessarily lead to estimate of the migration processes occurring in real food products. The greatest styrene levels was observed with ethanol 100% at 40°C for 24 h. However, at 70°C for the same period, the greatest styrene levels were observed in the case of decanol. The styrene concentration in the 3.5% fat milk is assumed to be comparable to that of the 20% ethanol at 40°C after 24 hours. The migration of styrene into hot beverages was more than the cold ones and was affected by contact time of contact.

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الملخص العربى

تقدير الاستيرين فى بعض المواد الغذائية وبعض مشابهات الأغذية والمنتقل من عبوات البولى إستيرين

رمزى بسيونى عبدالعزيز جمعه
معهد بحوث تكنولوجيا الأغذية
قسم هندسة تصنيع وتعبئة وتغليف الأغذية

تم تقدير تركيز الأستيرين المنتقل من عبوات البولى أستيرين إلى بعض المشروبات الباردة مثل (عصير البرتقال ، عصير التفاح ، الكولا وسفن أب) وبعض المشروبات الساخنة مثل (الشاى والقهوة ومشروب الكاكاو) والماء المقطر ، واللبن بنسب دهن مختلفة (٠,٥ ، ١,٥ ، ٣,٥%) دهن وبعض الأغذية مثل الجيلى والأيس كريم بالإضافة إلى بعض مشابهات الأغذية مثل ٣% حامض خليك ، ٨ ، ٢٠ ، ٥٠ ، ١٠٠ ، إيثانول ، ديكانول.

وجد أن معدل هجرة مركب الاستيرين يتأثر بنسبة الدهن ، وفترة التخزين ، ودرجة حرارة التخزين فيزداد معدل هجرة الاستيارين بزيادة نسبة الدهن ودرجة الحرارة والزمن.

فى حالة استخدام الماء المقطر كأحد المشابهات الغذائية كان معدل الهجرة أقل عنه فى حالة الأغذية الدهنية ، وفى حالة الإيثانول ٢٠% كان معدل الهجرة تقريبا يساوى معدل هجرة الاستيرين فى حالة اللبن ٣,٥% دهن. وكان أعلى معدل هجرة للاستيرين فى حالة ١٠٠% إيثانول على درجة ٤٠°م لمدة ٢٤ ساعة عن باقى المشابهات المستخدمة ، ولكن فى حالة رفع درجة الحرارة إلى ٧٠°م لنفس فترة التخزين (٢٤ ساعة) أعطى المشابهة ديكانول أعلى معدل هجرة عن باقى المشابهات المستخدمة. أيضا فى حالة المشروبات الساخنة كان معدل هجرة وانتقال الاستيرين دائما أكبر منه فى حالة المشروبات الباردة المستخدمة فى الدراسة.