

# Polystyrene Sheet Composition and Temperature as Parameters for Migration of Styrene Monomer into Corn Oil

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Different types of polystyrene used in packaging were tested for styrene monomer migration into corn oil. Several blends of general-purpose polystyrene with different amounts of high-impact polystyrene demonstrated a linear increase of migration of styrene with increasing amount of high-impact polystyrene in the polymer. Faster migration was found for higher exposure temperatures. Migration depended linearly on the content of residual styrene monomer in the polymer.

*Keywords:* Polystyrene; food packaging; sheet composition; temperature; styrene monomer content.

## INTRODUCTION

Polystyrene (PS) is frequently used for packaging of foods. Examples of general-purpose polystyrene (GPPS) are foamed trays for meat and clear trays for salads and vegetables. Examples of high-impact polystyrene (HIPS), which consists of a PS matrix with a dispersed rubber phase, are packages for margarine and dairy products such as yoghurts. Migration from packaging materials is influenced by a number of variables:<sup>1</sup>

- the physical and physico-chemical properties of the polymer (e.g. density, crystallinity, branching, composition, surface roughness).
- the manufacturing process of the packaging material (extrusion, injection-moulding, blow moulding, deep-drawing);
- the physical and physicochemical properties of the mobile component (migrant) of the packaging

material (e.g. molecular weight, polarity, solubility);

- the composition of the packaged product (e.g. fat or water content).

A model to predict the migration of components into oil at constant temperatures has been proposed by Reid *et al.*<sup>2</sup>

$$M_t = 2C_0 \sqrt{\frac{Dt}{\pi}} \quad (1)$$

where  $M_t$  is the mass of migrant migrated from polymer in time  $t$ ,  $C_0$  is the original concentration of the migrant in the polymer,  $t$  is the time and  $D$  is the diffusion coefficient of the migrant in the polymer. The model was applied to the migration of dioctyladipate from polyvinylchloride<sup>3</sup> and to the migration of styrene monomer from PS.<sup>4</sup> Also, Figge and coworkers<sup>7-9</sup> proposed a model at con-

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stant temperatures. The temperature dependence of diffusion is generally described by an Arrhenius type of correlation.<sup>3,5,6</sup>

$$D = A \cdot e^{-E/RT} \quad (2)$$

where  $D$  is the diffusion coefficient of the migrant in the polymer,  $T$  is the absolute temperature,  $R$  is the general gas constant,  $E$  is the activation energy and  $A$  is a constant.

From equations 1 and 2 a more general model for the prediction of migration can be derived

$$M_t = 2C_0 \sqrt{\frac{t}{\pi}} \cdot \sqrt{Ae^{-E/RT}} \quad (3)$$

which reduces to

$$M_t = KC_0 \sqrt{te^{-E/RT}} \quad (4)$$

where  $K$  is a complex constant.

The present study describes the migration of residual styrene monomer from different types of PS into corn oil. The influence of the amount of HIPS in several blends with GPPS and the effect of reduced contents of monomer in the polymer on the migration of styrene was investigated using both the immersion sampling method and the cell sampling method.<sup>10</sup> The influence of temperature on the migration of styrene monomer from a 1:1 blend of HIPS and GPPS was evaluated by the cell sampling method only.

## MATERIALS AND METHODS

### Materials

General-purpose polystyrene (GPPS: type Styron<sup>®</sup> 637 from Dow Chemical Company), high-impact polystyrene (HIPS: type Styron<sup>®</sup> 472 from Dow Chemical Company) and blends of both containing 3, 5, 10, 25, 50 and 75% HIPS were extruded into sheets of 1 mm thickness at ca. 220°C by Dow Benelux NV, Terneuzen, The Netherlands. The batch included also a range of 1 mm thick sheets of a 1:1 blend of GPPS and HIPS with reduced styrene monomer contents (see Table 2). Corn oil (Mazola) was bought in a local store at Wageningen (The Netherlands).

### Sample preparation

The high-impact-grade polystyrene sheets were cut into the pieces necessary for sampling with a pair of scissors. For sampling in GPPS and in the blends of HIPS with GPPS containing 3% and 5% HIPS, the sheets were scratched with a sharp object and subsequently broken over the scratch.

### Sampling methods

The influence of both the amount of HIPS in PS and the content of residual monomer in the polymer was evaluated by using the immersion sampling method and the cell sampling method.<sup>10</sup> For immersion sampling, a 1 dm<sup>2</sup> polystyrene sheet was cut into nine equal pieces, immersed in 50 g of corn oil in a tightly closed jar (all-sided contact) and incubated at 40°C.

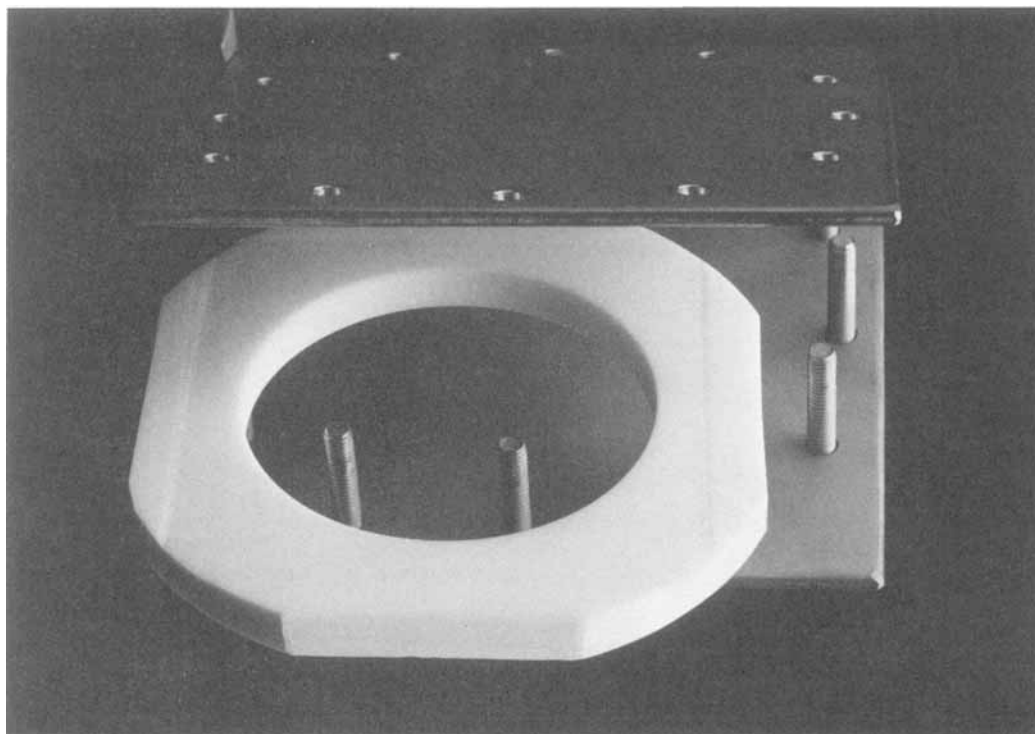
Cells for sampling were made of a 10.8 mm thick Teflon ring with an inner diameter of 80.0 mm (Figure 1). The Teflon ring was sandwiched between two stainless-steel plates in analogy with Figge.<sup>13</sup> Two sheets of polystyrene were secured between the ring and plates in such a way that different sides of each sheet were in contact with the corn oil. Cells were filled with 50 g of corn oil, tightly closed and incubated at 40°C.

Using the cell sampling method, sheets of a 1:1 blend of GPPS and HIPS of 1 mm thickness were incubated at 10, 20, 30, 40 and 50°C for evaluation of the effect of temperature on styrene migration.

### Styrene analysis

Residual styrene monomer was determined in the PS sheets by dissolving the polymer in dichloromethane and subsequently precipitating with iso-octane. The clear upper layer was analysed with a gas chromatograph (Carlo Erba, model 4200) equipped with a flame ionization detector. The analyses were carried out on a 15 m × 0.53 mm (i.d.) wide-bore column (DB 225, J & W Scientific). The detection and injection temperature were 300°C and 250°C, respectively. The following temperature programme was used: an initial hold for 2 min at 40°C and then 5°C/min to 100°C and a final temperature hold for 2 min.<sup>11</sup>

Styrene monomer in corn oil was determined by azeotropic distillation with methanol followed by



**Figure 1.** Sampling cell

extraction with pentane. The pentane extract was analysed with a gas chromatograph (Carlo Erba, model 4160), equipped with a flame ionization detector and a cold on-column injector. The analyses were carried out on a 30 m  $\times$  0.32 mm (i.d.) fused-silica capillary column (DB 1701, J & W Scientific). The detection temperature was 280°C. The following temperature programme was used: an initial hold of 4 min at 40°C and then 5°C/min to 90°C, followed by 15°C/min to 190°C and a final temperature hold for 1 min. A calibration curve was prepared by adding different amounts of styrene to the oil.<sup>12</sup>

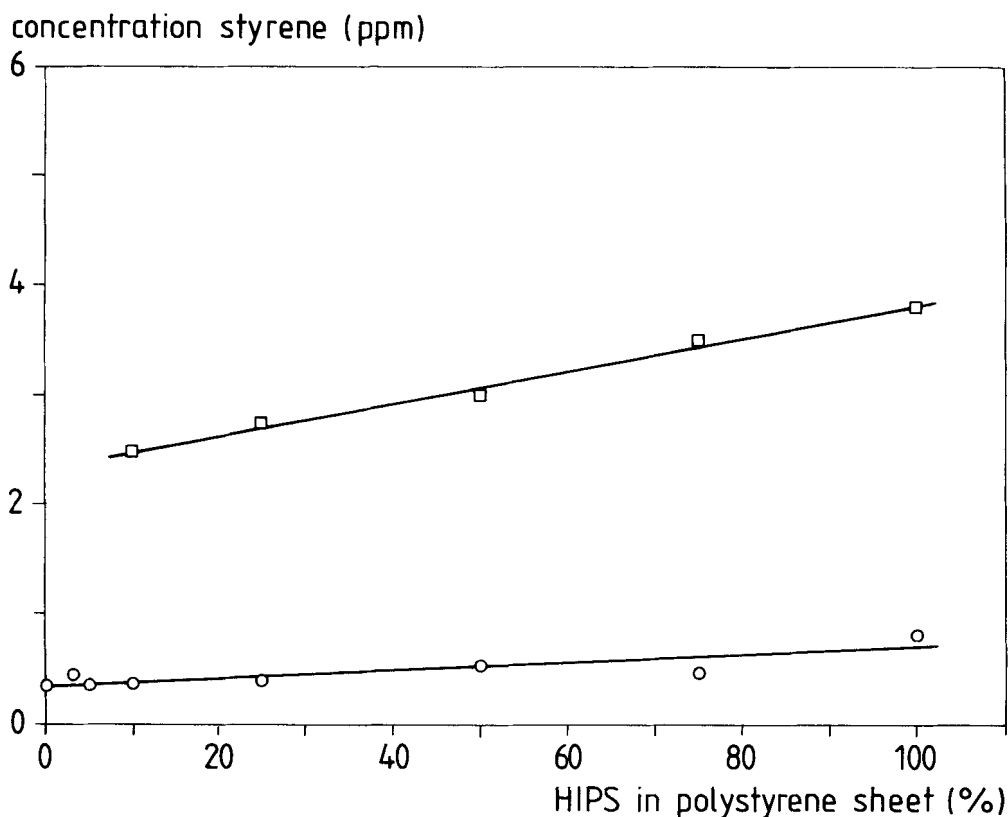
## RESULTS AND DISCUSSION

The contents of residual styrene monomer for the different PS samples were  $285 \pm 6$  ppm ( $n = 8$ ),

except for those with a reduced monomer content (see Table 2).

### Influence of different amounts of HIPS

Figure 2 shows the content of migrated styrene monomer in corn oil versus the amount of HIPS in several blends with GPPS. Migration increases linearly with increasing amounts of HIPS present in the polymer sample in both the immersion sampling method and the cell sampling method. Obviously diffusion of styrene monomer in the polymer increases with increasing amounts of rubber particles in the polymer blends of GPPS and HIPS. Immersion sampling results in higher amounts of migrated styrene (level and slope), possibly owing to damage of the rubber particles in the cut edges at the surface of the polymer promoting styrene transfer. Therefore, sampling cells give a



**Figure 2.** Effect of % HIPS in PS on the level of styrene migrated into corn oil after 21 days at 40°C using the immersion (□) and the cell (○) sampling method

more accurate representation of the migration behaviour in actual packaging applications. These findings confirm previous work.<sup>10,14</sup>

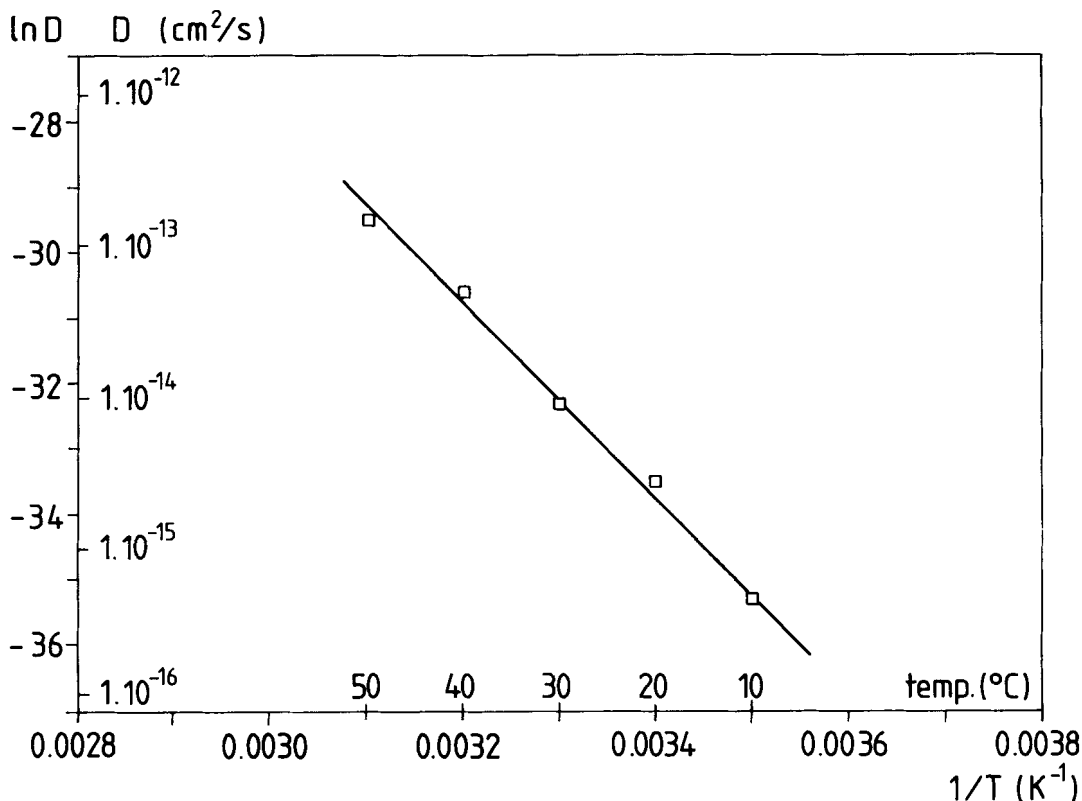
40°C. Miltz and Rosen-Doody<sup>16</sup> calculated a  $D$  value of  $5 \times 10^{-10}$  cm<sup>2</sup>/s for PS containing 1000 ppm residual monomer at 35°C. However, the latter value is too high, because their method

### Temperature dependence

Table 1 gives the amounts of styrene migrated from 1 mm thick sheets of a 1:1 blend of GPPS and HIPS into corn oil after 14 days of incubation at different temperatures. The diffusion coefficient  $D$  was calculated for each temperature using Equation 1. Table 1 shows that the diffusion coefficient increases with increasing temperature from  $4.7 \times 10^{-16}$  cm<sup>2</sup>/s at 10°C to  $1.5 \times 10^{-13}$  at 50°C. By comparison, Till *et al.*<sup>4</sup> reported  $D$  values of 2–5 ( $\times 10^{-13}$ ) cm<sup>2</sup>/s for GPPS with a residual styrene monomer content of 800 ppm at 40°C. Snyder and Breder<sup>15</sup> found  $D$  values of 2–3 ( $\times 10^{-13}$ ) cm<sup>2</sup>/s for GPPS with a monomer content of 4260 ppm at

**Table 1.** Migrated amounts of styrene monomer and diffusion coefficients ( $D$ ) for styrene in polystyrene ( $C_0 = 279$  ppm) in contact with corn oil in a cell at different temperatures ( $T$ ) after 14 days

$T$ (°C)	Migrated amount of styrene ( $\mu\text{g}/\text{cm}^2$ )	$D$ (cm <sup>2</sup> /s)
10	0.0075	$4.7 \times 10^{-16}$
20	0.0188	$2.8 \times 10^{-15}$
30	0.0333	$0.9 \times 10^{-14}$
40	0.0773	$5.1 \times 10^{-14}$
50	0.1388	$1.5 \times 10^{-13}$



**Figure 3.** Diffusion coefficient ( $D$ ) of styrene in PS (HIPS:GPPS 1:1) as a function of temperature as obtained from migration into corn oil

assumed already an equilibrium of styrene between polymer and contacting phase in an early stage. Using Equation 2,  $\ln D$  vs.  $1/T$  can be plotted in which  $E/R$  is the slope of the line. Figure 3 shows this relationship obtained from migration of styrene into corn oil. Linear regression results in

$$\ln D = 15.61 - 14\,500 (1/T) \quad (r = 0.99)$$

So,  $E/R = 14\,500$  and the activation energy calculated is  $12.0 \times 10^4$  J/mol. This is near the activation energy of  $7.8 \times 10^4$  J/mol found for styrene migration in cut test coupons made of pressed GPPS.<sup>4</sup> The complex constant  $K$  from Equation 4 can be calculated from the activation energy found and the results of Table 1. A value of  $K = 2620 \pm 323$  cm s<sup>-1/2</sup> ( $n = 5$ ) was obtained. Equation 4 represents now a general formula for predicting the migration of styrene monomer from polystyrene (GPPS:HIPS = 1:1) into corn oil.

#### Effect of content of residual styrene monomer

Table 2 presents the effect of different contents of residual monomer on the migration of styrene into corn oil from a sheet of a 1:1 blend of GPPS and HIPS incubated at 40°C for 21 days. It demonstrates once more that sampling in migration cells results in much lower levels of migrated styrene than with immersion sampling. The cell sampling method shows about the same ratio for all the PS samples, which indicates a linear dependency between the contents of styrene in the polymer and the level of styrene migrated into corn oil. However, for immersion sampling this ratio is only similar for the PS samples with the three highest contents of styrene. The PS samples with the two lowest amounts of styrene in the polymer show increasing ratios between the contents of styrene in the poly-

**Table 2. Contents of styrene in polystyrene samples (GPPS:HIPS 1:1) and contents of styrene in corn oil after 21 days of migration at 41°C using different sampling methods and the ratio between these contents**

Styrene content in polystyrene (ppm)	Immersion sampling Styrene content in oil (ppb)	ratio	Cell sampling Styrene content in oil (ppb)	ratio
279 ± 4	2790	100	354	788
191 ± 5	2010	95	246	776
164 ± 4	1590	103	210	781
93 ± 2	660	141	120	775
42 ± 2	120	350	54	778

<sup>a</sup>Values are means of triplicates ± SD.

mer and the levels of styrene migrated into corn oil. Less styrene seems to be available for migration, especially from the cut edges. At a certain concentration of monomer, much less styrene is available for initial leakage from the rubber particles after cutting of the polymer.<sup>10</sup>

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