

Kinetics of Styrene Removal from Polystyrene by Thermal Treatment in Air

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Synopsis

The influence of certain factors on the kinetics of styrene mass transfer from polystyrene in air at elevated temperature is investigated. It is established that this process can be simulated by a model including molecular diffusion of styrene to the surface of the solid material and evaporation from that surface. The effective coefficients of molecular diffusion at different temperatures and the evaporation coefficients under different hydrodynamic conditions are determined. The data obtained can be used for estimation of the monomer removal by thermal treatment of the polymer.

INTRODUCTION

From theoretical and practical points of view, the kinetics of monomer mass transfer from polystyrene in air at elevated temperature is of great interest. Such transfer is expected to take place both in the polymer granulation and in the granulate processing into products. Depending on the rate of the process, on one hand, the monomer contents in the product will change, which is of great importance when it is used for food packaging, and on the other hand, the surroundings will be polluted with styrene to different extents.

Studies on this matter carried out so far¹⁻³ are insufficient to predict the rate of the process, since the monomer in them is removed by a liquid with undefined hydrodynamics.

Under these circumstances we set ourselves the task of studying the kinetics of styrene transfer from polystyrene in air at elevated temperature.

THEORY

Monomer transfer in the gas phase around the polystyrene is expected to comprise two stages: diffusion of styrene to the surface of the polymer, and evaporation of the monomer from the surface into the gas phase. Should this mechanism be assumed, the process of transfer from an infinite plane sheet of polystyrene will be described by the differential equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

with a boundary condition

$$-D \frac{\partial C}{\partial x} = \alpha(C_s - C_o) \quad (2)$$

If the styrene initial distribution in the sheet is uniform, the total amount of the monomer leaving the sheet up to time t of contact with the gas phase will be expressed by the equation

$$M_t = M_\infty \left[1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 Dt/l^2)}{\beta_n^2 (\beta_n^2 + L^2 + L)} \right], \quad (3)$$

which results from the mathematical solution of Eq. (1) at the boundary condition (2).⁴

In the above expression β_n are the positive roots of the equation

$$\beta \operatorname{tg} \beta = L = l\alpha/D \quad (4)$$

The evaporation coefficient α depends mainly on the hydrodynamic conditions in the surrounding fluid.⁵ At sufficiently large gas flow rates $\alpha \gg D$ and $L \rightarrow \infty$. Then the mass transfer rate will be determined entirely by the diffusion in the sheet and Eq. (3) is transformed⁴ into

$$M_t = M_\infty \left\{ 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right] \right\} \quad (5)$$

This equation is used quite often to determine the effective molecular diffusion coefficient in polymers. Normally, long times of contact are selected so that only the first term of the expansion must be used. If M_t and M_∞ are expressed by the initial monomer concentration C_i and its average concentration C' in the sheet, taking the logarithm yields

$$\ln \frac{C'}{C_i} = \ln \frac{8}{\pi^2} - \frac{D\pi^2}{4l^2} t \quad (6)$$

Using the above equations and appropriate experiments makes possible the determination of the molecular diffusion coefficient and the coefficient of evaporation, needed for estimation of the process.

EXPERIMENTAL

In order to study the process, plates of impact-resistant polystyrene Bustrone with length 40 mm, width 20 mm, and thickness 1.7 mm were utilized. They were put into a glass tube with regulated external heating. The flow rate of the air passing through it was measured with a rotameter. The desired temperature of the air before and behind the sheet was obtained by varying the voltage applied to the heater coil. At definite time intervals the average contents of styrene in the sheets was measured. For this purpose they were dissolved in dichloromethane and the solutions obtained were analyzed in a chromatographic system Perkin Elmer (gas chromatograph Sigma 3B and

chromatography data station Sigma 10B). The operating conditions were:

A glass column 2 m in length, inner diameter (i.d.) 3 mm, packed with 20% dinonylphthalate on Gas Chrom Q;

Column temperature: 110°C;

Injector temperature: 150°C;

Detector temperature: 200°C.

The method sensitivity was 3 ppm styrene and the variational coefficient was 3.7 per cent.

The air temperature around the sheets was varied from 40°C to 80°C and the air flow rate at 20°C varied from 20 L/h to 400 L/h. Under these circumstances the Reynolds number in the tube, Re , was varied from 16.9 to 373. On increasing the gas flow rate above 400 L/h no acceleration of the process was observed which proves that the resistance of mass transfer from the sheet surface into the air is negligible compared to the diffusion resistance in the sheet.

Experiments were also carried out with sheets placed vertically in an air atmospheric drier, ensuring free air convection. A series of experiments was performed in a vacuum drier at residual pressure of 0.1 bar.

RESULTS AND DISCUSSION

The values of the effective molecular diffusion coefficient at the temperatures of interest were determined as a first approximation by the least-squares method from the slope of a plot of $\ln(C'/C_i)$ vs. t , Eq. (6), using the data for a gas flow rate of 400 L/h. After a procedure controlled by least-squares treatment for fitting of these data to Eq. (5) the following results were obtained: at $T = 40^\circ\text{C}$, $D = 10.9 \cdot 10^{-8} \text{ cm}^2/\text{sec}$; at $T = 60^\circ\text{C}$, $D = 13.3 \cdot 10^{-8} \text{ cm}^2/\text{sec}$; at $T = 80^\circ\text{C}$, $D = 15.1 \cdot 10^{-8} \text{ cm}^2/\text{sec}$. Figure 1 illustrates the experimental points compared to the curves calculated by eq. (5) using the above-cited values of D . The latter are commensurable in order of magnitude with the data about the molecular diffusion coefficient of low-molecular substances in polymers,⁶⁻⁹ but differ substantially from the values given in Ref. 1.

The activation energy of the diffusion process and the multiplier D_0 in the expression

$$D = D_0 \exp(-E/RT) \quad (7)$$

determined by our experiments are approximately $7.5 \cdot 10^3 \text{ KJ/Kmol}$ and $1.96 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ respectively.

Substituting the molecular diffusion coefficients in Eq. (3), the time dependence of the amount of styrene liberated (as a portion of the initial quantity in the polymer) was calculated for different values of L . The plots are presented in Figure 1. It is evident that at a flow rate of 80 L/h ($Re_{av} = 71$), natural convection and a vacuum of 0.9 bar, the results are nearly equal and correspond to $L \approx 20$. According to Eq. (4), this value corresponds to an

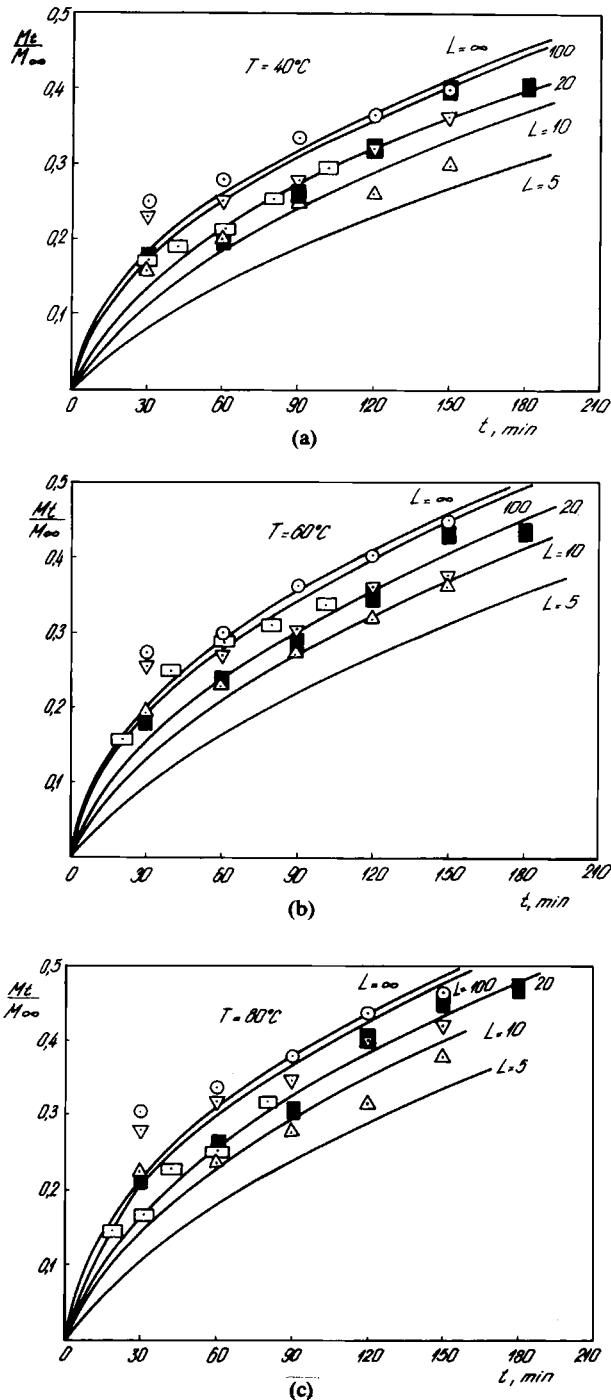


Fig. 1. Comparison between the experimentally determined relative decrease of the monomer contents in polystyrene and the decrease calculated by Eq. (3) for different values of L and temperatures (a) 40°C ; (b) 60°C ; (c) 80°C . ■, vacuum 0.9 bar; □, free convection; △, air flow rate 20 L/h; ▽, air flow rate 80 L/h; ○, air flow rate 400 L/h.

average evaporation coefficient $\alpha = 0.30 \cdot 10^{-4}$ cm/sec. When the flow rate is 20 L/h ($Re_{av} = 18$) the values, corresponding to it, are $L \approx 10$ and a twice smaller respective value of $\alpha = 0.15 \cdot 10^{-4}$ cm/sec.

It is seen from the figure that the theoretical curves for $L = 100$ and $L = \infty$ differ slightly. Therefore, at evaporation coefficients $\alpha \geq 1.3 \cdot 10^{-4}$ cm/sec ($Re_{av} \geq 360$) the resistance of the mass transfer process will be governed predominantly by the molecular diffusion of styrene in the polymer. The above condition in air flow in the temperature range of interest is fulfilled for gas velocities exceeding 0.32 m/sec. At lower rates the effect of evaporation of styrene from the surface of the material is enhanced. It is interesting to note that the influence of evacuation to 90 percent on the evaporation rate is analogous to the effect of free convection around the material.

For the temperatures and sheet thicknesses used in the experiments, a complete removal of styrene from the polymer requires a rather long thermal treatment which is obviously disadvantageous. However, the obtained values of the effective molecular diffusion coefficient and evaporation coefficient make it possible to analyze the effect of such treatment on much thinner products.

It can be seen from Figure 1 that the initial degree of monomer removal is higher than the theoretical one. This may be due to a departure of the real experimental conditions from those used for derivation of Eq. (3). For the next time intervals the agreement of the experimental data with the theoretical predictions is quite satisfactory.

CONCLUSIONS

The removal of styrene from polystyrene by thermal treatment in air is described satisfactorily by a model involving monomer molecular diffusion to the surface of the solid material and evaporation from the surface. The effective molecular diffusion coefficient at 40, 60, and 80°C and the evaporation coefficient under various hydrodynamic conditions are defined. At an air velocity above 0.32 m/sec the process resistance is dictated mainly by the molecular diffusion of styrene in the polymer. The effective diffusion coefficient is of the same order of magnitude as the diffusion coefficient of low-molecular substances in other polymers. The results obtained can be used for estimation of the monomer migration process in thermal treatment of the polymer or in storing materials in polystyrene packages.

NOMENCLATURE

C	Concentration of styrene in polystyrene, kg/m ³
C_0	Concentration of styrene in the polymer at equilibrium with the styrene bulk concentration in the gas phase, kg/m ³
C_s	Concentration of the monomer on the surface of the sheet, kg/m ³
C'	Average concentration of the monomer in the sheet, kg/m ³
C_i	Initial concentration of styrene in the sheet, kg/m ³
d	Inner diameter of the tube for thermal treatment of the sheets, m
D	Effective molecular diffusion coefficient of styrene in the polymer, m ² /sec
E	Activation energy of the diffusion process, KJ/Kmol

21	Thickness of the polystyrene sheet, m
L	Bio number ($L \equiv Bi = 1\alpha/D$), dimensionless number for evaluating the ratio between external and internal diffusion rates
M_∞	Initial quantity of styrene in the sheet, kg
M_t	Quantity of removed styrene from the sheet after a given time of thermal treatment, kg
R	Universal gas constant
t	Duration of the thermal treatment of the sheet, sec
w	Average gas velocity, m/sec
α	Coefficient of evaporation (mass transfer) from the sheet into the gas phase, m/sec
ν	Kinematic air viscosity, m ² /sec
Re	Reynolds number ($Re = wd/\nu$).

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