

Cooling Time and Some Barrier Properties of Polystyrene Foam

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Synopsis

A set of modified expandable polystyrenes was prepared, and the cooling time of the foam samples was measured in the mold during the processing. Polystyrene foam obtained was evaluated with respect to barrier properties. Steady state gas permeation and countercurrent gas binary diffusion were used for the determination of barrier characteristics of the foam. Effective permeabilities and effective diffusion coefficients obtained were correlated with the cooling time of the foams. The conclusive dependence of the barrier characteristics on the cooling time was found.

INTRODUCTION

The raw material used for preparation of molded bead foam consists of polystyrene particles with blowing agent trapped among the rigid chains. First, the particles are heated in a continuous flow of steam to yield partially expanded (preexpanded) particles of the desired density. After a maturing period of several hours during which the pressure inside the particles falls to atmospheric, the particles are heated in the mold by steam injected into the cavity, so that they expand to fill the interstices and fuse together. The last phase of the molding operation is a cooling by circulating cold water or air in the jacket of the mold until it is possible to take out the foam without damage. The cooling period is a time-consuming process, and it usually takes more than 70% of the total processing time in the mold. Therefore, great attention has been given to the reduction of the cooling period and effective methods have been found.

At present the cooling time reduction is achieved mostly by the addition of small amount of halogenated hydrocarbons or organic esters,¹⁻⁴ even though methods based on the special processing equipment are also known.⁵

However, the presence of "cooling time modifiers" affects the porous structure of the foam^{6,7} and hence some of its properties. It is known that fast-cooling foams show higher permeability for water vapor and gases and water absorption compared with conventional slow-cooling types. This "more opened" structure of fast-cooling foam may affect negatively thermoinsulating efficiency, some mechanical properties, etc.

There are two mechanisms of cooling a hot mold: heat conduction due to the temperature gradient and convection by hot gases (blowing agent, air, and steam) caused by pressure and concentration gradients. Supposing the porous structure formation is finished at the very beginning of the cooling

period, a relationship should exist between cooling time and barrier properties of the foam.

No systematic study dealing with such relationships has been published. In this contribution an attempt has been made to find a correlation between cooling time and transport characteristics of the foam obtained by gas permeation and gas diffusion measurements for a set of differently modified materials.

EXPERIMENTAL

Materials

Polystyrene beads used for sample preparation: Polystyrene $\overline{M}_v = 170,000$, determined from the intrinsic viscosity measurements at 30°C in toluene.⁸ Blowing agent: mixture of *n*-pentane and *i*-pentane 60/40: 6 wt %. Hexabromocyclododecane = 0.01–0.05 wt %; glycerine monostearate: 0.01–0.05 wt %.

Sample Preparation

Polystyrene beads were prepared by suspension polymerization, using dibenzoylperoxide as initiator. The suspension was stabilized by using 0.17 % of poly(vinyl alcohol) based on monomer. Hexabromocyclododecane was incorporated during polymerization at about 70% conversion. Glycerine monostearate was added to beads in the form of water emulsion and homogenized for 15 min in a slow running mixer.

The beads of size 1.25–2.50 mm were processed by the standard procedure in three steps.⁶ Preexpansion was carried out by steam having pressure 0.17 MPa in a batch laboratory preexpander. The preexpanded material was left 24 h in a ventilated space at 23°C and then heated again by 0.16 MPa steam for 20 s in the mold of standard construction. After that the mold was cooled by water of 15°C. Dimensions of the block were 30 × 20 × 10 cm. During the expansion the block temperature was continuously recorded by means of a thermocouple placed at 2 cm distance from the surface.

The foam block was conditioned for 30 days at room temperature in a ventilated space to remove blowing agent. Cylindrical specimens of 20.5 mm diameter and 25 mm height for gas permeability measurements were cut by a laboratory cork borer. The surface layers of the block were removed by a blade. All samples were cut off in the same place in the blocks. The samples were forced into a short cylindrical brass tube (Fig. 2) with inner diameter 20 mm and thereafter left to rest for 180 h. No significant systematic permeability changes occurred after this time period. For the measurements of binary gas diffusion the samples were forced into cylindrical holes (diameter 20 mm) of a metallic disc (thickness 20 mm), dividing the top and bottom part of the diffusion cell (Fig. 3.). The samples were conditioned in the disc for 180 h before measurement.

Measurements

Cooling time was taken as the time from the start of cooling by water to the moment of abrupt temperature fall (Fig. 1). The detailed procedure is given in the previous paper.⁷

Determination of the effective gas permeability coefficient B was made by the method of steady nitrogen permeation (Fig. 2). The volumetric flow rate of nitrogen \dot{V} is measured by a soap-bubble flow meter on the outlet from the bottom face of the sample. Because the pressure at the bottom face is atmospheric (p), the pressure difference Δp necessary to force nitrogen through the sample is measured by an open U-tube pressure gauge, filled with silicone oil, placed above the upper face of the sample. The effective permeability coefficient B is defined by the d'Arcy equation

$$N = B (\Delta p / R_g T L) \quad (1)$$

where N is nitrogen molar flux density (mol/cm² s) determined from volumetric flow rate \dot{V} (cm³/s) according to

$$N = \dot{V} p / R_g T S \quad (2)$$

where S is the cross section of the cylindrical sample, R_g the gas constant, T temperature, and p pressure. All measurements were made at the same average pressure in the sample, and it is therefore possible to compare directly B calculated from eq. (1).

Steady gas counter diffusion in the binary system H₂-N₂ was measured in a diffusion cell showed in Figure 3 and described in detail elsewhere.⁹ According to Graham's law the ratio of molar flux densities of hydrogen

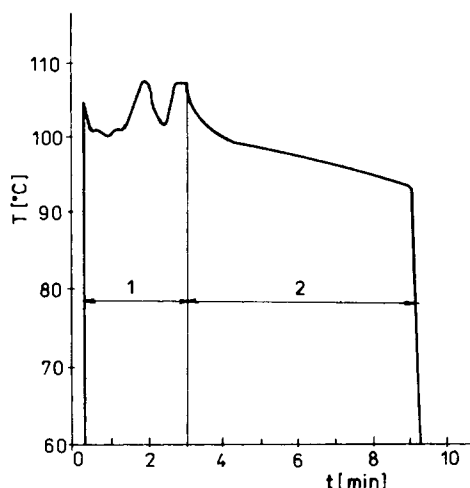


Fig. 1. Temperature time profile inside the polystyrene foam block during expansion: (1) heating by steam; (2) cooling.

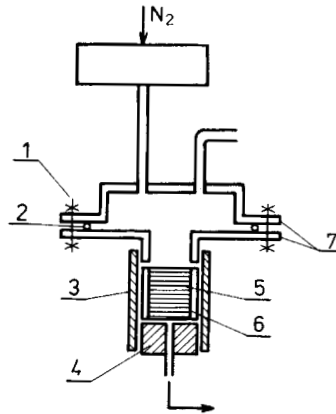


Fig. 2. Scheme of apparatus for steady state permeation of nitrogen: (1) bolts; (2) sealing ring; (3) rubber tube; (4) rubber plug; (5) polystyrene sample; (6) brass tube; (7) metal flanges.

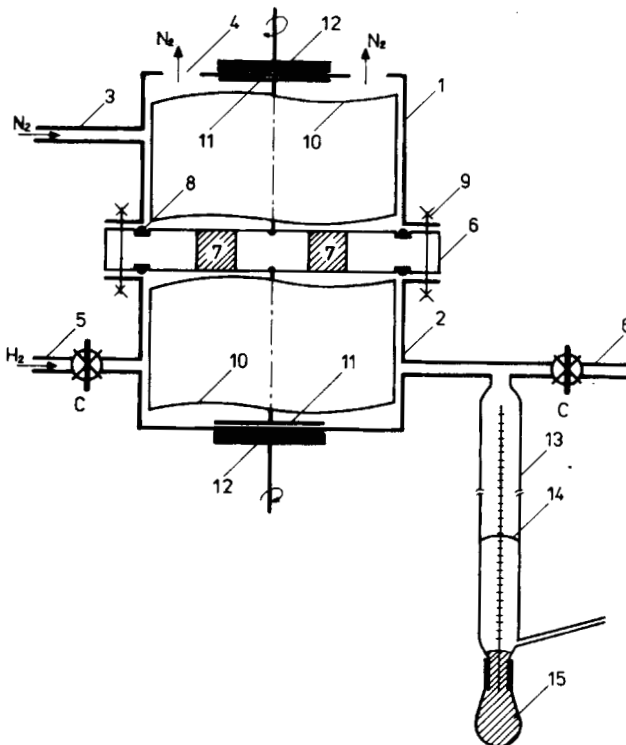


Fig. 3. Scheme of diffusion cell: (1,2) upper and bottom metallic parts of cell; (3,4) inlet and outlet of nitrogen; (5,4) inlet and outlet of hydrogen; (6) circular metallic disc with openings for samples; (7,8) O-rings; (9) bolts; (10) stirrer blades; (11) metallic plate; (12) rotating magnet; (13) calibrated burette; (14) soap film; (C1, C2) glass stopcocks (position of stopcocks corresponds to measurement).

and nitrogen in a porous material at isobaric condition equals

$$N_H / N_N = (M_N / M_H)^{1/2} = 3.74 \quad (3)$$

where M_i is the molecular weight ($i = H, N$). Diffusion through a sample is thus nonequimolar and the total diffusive flux ($N = N_H - N_N$) can be followed according to the rate of the upward motion of the soap film in a burette joined to the bottom part of the cell filled by hydrogen before measurement. Nitrogen flows through the upper part of the cell during the whole measurement. In order to get perfect mixing magnetic blade stirrers were used in both parts of the cell. The hydrogen diffusion flux density N_H is determined from the rate of volume change in the bottom part of the cell

$$N_H = 1.37 \dot{V}_p / R_g T S \quad (4)$$

where p and T are atmospheric pressure and temperature and S is the cross section of samples placed in the metallic disc. The effective diffusion coefficient of hydrogen in binary system H_2-N_2 , D , is defined by Fick's law, which for given conditions can be written

$$N_H = D(p / R_g T)(\Delta Y_H / L) = D(p / R_g T)(1 / L) \quad (5)$$

where L is the sample thickness and ΔY_H the difference of mole fractions of hydrogen in the bottom part and top part of the cell ($\Delta Y_H = 1 - 0 = 1$).

RESULTS AND DISCUSSION

For the study of relations between cooling time of polystyrene foam and its barrier properties by gas permeation only small parts of the original molding are used. To judge the homogeneity of the foam, the coefficients B for a set of samples from different places of the mold were determined. The results in Table I show a broad variation of B characterized by a variation coefficient. Because the variation coefficient of the experimental permeability measurement is less than 1%, the scatter of B must be due to mold heterogeneity. This is in a good agreement with the determination of polystyrene foam density, which shows broad fluctuation in the mold.¹⁰

It is interesting that foam permeability has no direct connection with foam heterogeneity; small variation coefficients were found even at high values of B .

The variation coefficient of t_c is about 10–15% for cooling times 3–8 min, as proved by repeated measurements. For very short cooling time (under 3 min) the standard deviation is higher, but not over 0.5 min.

In spite of the heterogeneity of the polystyrene foam a systematic dependence of permeability coefficients on the mold cooling time was found (Fig. 4). The response of permeability to changes of cooling time is remarkably strong. For example, the cooling time reduction from 4.9 to 1.75 min, i.e., by 64%, coincides with the permeability coefficient increasing from 32 to

TABLE I
 Permeability Coefficients of Nitrogen

Block	<i>B</i> for individual samples	Average value* <i>B</i> (cm ² /s)	Standard deviation <i>s</i> (<i>B</i>) (cm ² /s)	Variation coefficient <i>s</i> (<i>B</i>)/ <i>B</i> (%)
1	10.0; 26.6; 6.41; 7.55	12.6	9.4	75
2	30.2; 18.2	24.2	8.5	35
3	34.6; 30.0; 10.4; 24.0	24.8	10.5	42
4	33.8; 29.7	31.4	2.9	7
5	43.1; 36.0	39.6	5.0	13
6	90.4; 56.1	73.3	24.3	33
7	78.4; 71.6	75.0	4.8	6
8	96.0; 91.1	93.6	3.5	4
9	186.6; 93.7; 146.3	142.2	46.6	33
10	339.7; 324.0; 235.8; 336.2	308.9	49.2	16
11	382.3; 457.1	419.7	52.9	13
12	556.2; 660.3	608.3	73.6	12

*Average value from 7–10 measurements.

420 cm²/s⁻¹, i.e., by 1200%. This strong dependence of *B* on cooling time *t_c* or cooling time constant 1/*t_c* confirms the earlier result of Pogany¹¹ and Skinner and Eagleton,¹² who supposed the transport of hot gases from the mold as the prevailing mechanism of cooling.

The changes of barrier properties of the polystyrene foam with reduction of cooling time were confirmed also by gas diffusion measurements. The

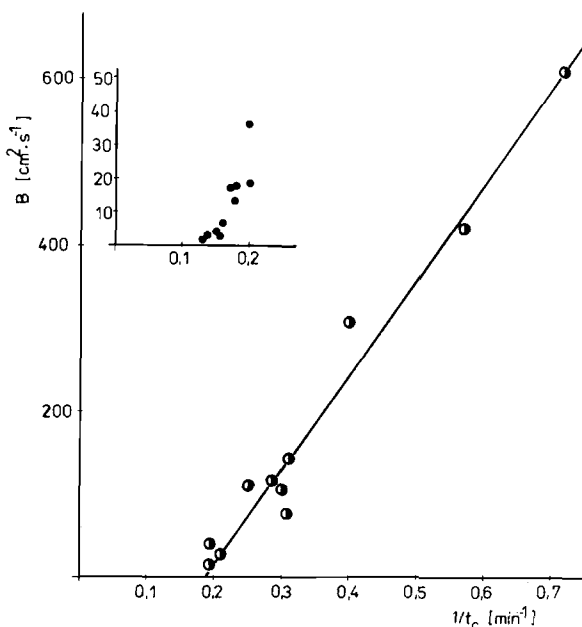


Fig. 4. Nitrogen effective permeability coefficient *B* vs. cooling time constant 1/*t_c*.

dependence of the effective hydrogen diffusion coefficient D on cooling time constant $1/t_c$ (Fig. 5) shows linear correlation between these parameters. Because diffusivity D is not so extremely sensitive to the cooling time as permeability, the diffusion method seems to be more useful for practical purposes.

The different sensitivity of B and D on cooling time indicates a presence of flow openings in the foam which bring about both permeation and diffusion of gases. According to the Hagen-Poiseuille equation a permeability coefficient depends on the effective flowthrough cross section ψ as well as on the size of the flowthrough openings (r^2). In the case of molecular diffusion the diffusion coefficient depends on ψ only. A conclusion can be made that changes of porous structure caused by the presence of cooling time modifiers increase both ψ and r . Far greater permeability sensitivity to cooling time ($B \sim \psi, r^2$) than that for diffusivity ($D \sim \psi$) is the result of these changes.

Knowledge of these transport characteristics does not permit us to decide if the flowthrough openings are spaces between expanded polystyrene beads or if they are holes in the wall membranes.

Further study, including determination of foam morphology by optical methods and influence of modifiers on the structure formation of foam, is in progress.

CONCLUSIONS

Based on measurements of cooling time, gas permeation, and gas diffusion for a set of modified polystyrene foams, we can conclude that:

1. The shorter the cooling time of the foam molding, the greater is its permeability for gases.
2. The transport of hot gas mixtures from the mold due to pressure and concentration gradients is the dominant mechanism of cooling.

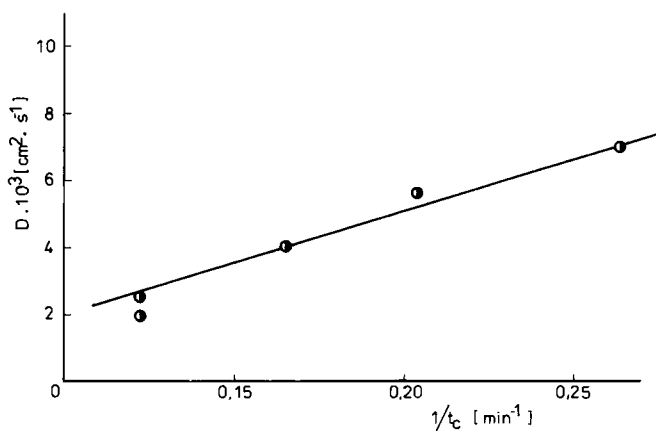


Fig. 5. Hydrogen effective diffusion coefficient D in binary system H_2 - N_2 vs. cooling time constant $1/t_c$.

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