

TRANSIENT DIFFUSION OF GASES IN POLYMER FOAMS HAVING NON-UNIFORM DENSITY

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ABSTRACT

Transient gas diffusion through closed-cell polymeric foams varies with boundary and initial conditions, which affect the local foam concentration for both constant and variable diffusion coefficients. In order to determine the solution for transient gas diffusion with variable diffusion coefficients, a new approach, implicit numerical solution, has been adopted using the Thomas algorithm to solve the tri-diagonal matrices. The one-dimensional diffusion equation, neglecting accumulation and depletion of volatile solute in the non-crystalline polymer fraction was used to develop the model. The results produced are equivalent to those predicted by the Fourier series solution for a polymeric foam having uniform density.

BACKGROUND

A critical literature review on various properties and the diffusion process of rigid cellular foams indicated that the study on thermal aging and evaluation of the physical properties had been confined to the closed-cell foams of constant density. Various models for predicting the physical parameters of rigid cellular foams and experimental methods for the measurement of these parameters have been developed at isothermal conditions for foams having uniform density and cell structure. The prediction of aging characteristics for foams having locally variable density has not been developed comprehensively. The need for further development of a model for the prediction of physical properties for the foams having variable density should be considered along with validation methods.

OBJECTIVES OF PAPER

The purpose of this paper is to discuss a mathematical model developed to predict the transient local gas pressure with variable diffusion coefficients, resulting from inward diffusion of air components and outward diffusion of a blowing agent at defined environmental conditions using a finite difference numerical solution.

MATHEMATICAL MODEL

A solution of the transient diffusion equation has been developed using an implicit finite difference method by solving the system of simultaneous equations described by a tri-diagonal coefficient matrix [1]. Fundamental comparisons of the analytical and numerical solutions of the diffusion equation for cellular plastic foam structure can be made from component partial pressure profiles obtained from the two techniques. The implicit method has been used because the large set of simultaneous algebraic equations is solved, overcoming the difficulties of more complicated computational procedures. The implicit

method consists of representing u_{xx} by a finite-difference form evaluated at the advanced point of time t_{n+1} , instead of at t_n as in the explicit method. In the analytical method, the solution for the total amount of diffusing substance which has entered the foam at time t and the corresponding quantity after infinite time is developed [2].

Analytical Method

In the analytical method, the classical Fourier series solution [2] for the case of one-dimensional diffusion in a polymer foam is traditionally used. If the region $-l < x < l$ is initially at a uniform concentration c_0 for polymer foam having $2l$ thickness, and the surfaces are kept at a constant concentration c_1 , the solution becomes

$$\frac{c - c_0}{c_1 - c_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left\{-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right\} \cos \frac{(2n+1)\pi x}{2l} \quad (1)$$

Initial and boundary conditions for the case of the polymer foam filled with 1 atm pressure of blowing agent stored in an oxygen/nitrogen atmosphere are

Initial Conditions:

$$\begin{aligned} @ t \leq 0, -l < x < l, \quad c &= 0.0 \text{ for O}_2 \text{ and N}_2 \\ &= 1.0 \text{ for blowing agent} \end{aligned}$$

Boundary Conditions:

$$\begin{aligned} @ t > 0, x = \pm l, \quad c &= 0.79 \text{ for N}_2 \\ &= 0.21 \text{ for O}_2 \\ &= 0.0 \text{ for blowing agent.} \end{aligned}$$

Implicit Numerical Method

An implicit numerical method for solving the diffusion of gases in the polymer foam is developed in the research [3]. The Thomas algorithm [1] is used for the solution of equations resulting from application of the implicit form.

It is convenient to use dimensionless independent variables, so by introducing

$$\lambda = \frac{\Delta \tau}{(\Delta X)^2}, \quad \tau = \frac{D_0 t}{L^2}, \quad X = \frac{x}{L}, \quad C = \frac{c}{c_0}, \quad f_x = \frac{D}{D_0}$$

The one-dimensional diffusion equation [4] with variable diffusion coefficient is,

$$\frac{\partial c}{\partial t} = \frac{\partial^2 (D, c_i)}{\partial x^2} \quad (2)$$

The dimensionless form of Equation (2), the one-dimensional diffusion, becomes

$$\frac{\partial C}{\partial \tau} = f_x \frac{\partial^2 C}{\partial X^2} + \frac{\partial C}{\partial X} \frac{\partial f_x}{\partial X} \quad (3)$$

where λ is (scaled age)² [5] and τ is the diffusion Fourier number.

The expression for f_x of a quadratic variation in density with position is given as $f_x = a + bX + cX^2$.

The backward finite-difference form of Equation (3) becomes

$$-\lambda f_x C_{i-1,n+1} + (I + 2\lambda f_x + \Delta f_x) C_{i,n+1} - (\lambda f_x + \Delta f_x) C_{i+1,n+1} = C_{i,n}. \quad (4)$$

This results from using

$$\frac{\partial C}{\partial \tau} = \frac{C_{i,n+1} - C_{i,n}}{\Delta \tau}, \quad (5)$$

$$\frac{\partial C}{\partial X} = \frac{C_{i+1,n+1} - C_{i,n+1}}{\Delta X}, \quad (6)$$

$$\frac{\partial^2 C}{\partial X^2} = \frac{C_{i-1,n+1} - 2C_{i,n+1} + C_{i+1,n+1}}{\Delta X^2}, \quad (7)$$

$$\text{and } \frac{\partial f_x}{\partial X} = \frac{f_{x_{i+1,n+1}} - f_{x_{i,n+1}}}{\Delta X}. \quad (8)$$

The solution of the M-1 linear equations which result at each time step become

$$(I + 2\lambda f_x + \Delta f_x) C_{1,n+1} - (\lambda f_x + \Delta f_x) C_{2,n+1} = C_{1,n} + \lambda f_x g_0(t_{n+1}) \quad (9)$$

$$-\lambda f_x C_{i-1,n+1} + (I + 2\lambda f_x + \Delta f_x) C_{i,n+1} - (\lambda f_x + \Delta f_x) C_{i+1,n+1} = C_{i,n} \quad (10)$$

for $2 \leq i \leq M-2$

$$-\lambda f_x C_{M-2,n+1} + (I + 2\lambda f_x + \Delta f_x) C_{M-1,n+1} = C_{M-1,n} + (\lambda f_x + \Delta f_x) g_1(t_{n+1}). \quad (11)$$

The boundary and initial conditions are:

$$C_{0,n+1} = g_0(t_{n+1}) \quad (12)$$

$$C_{M,n+1} = g_1(t_{n+1}) \quad (13)$$

$$C_{i,0} = f(x_i). \quad (14)$$

RESULTS AND DISCUSSION

Uniform Foam Density Distribution

Predicted Transient Partial Pressure Profiles

Comparison of model predictions of blowing agent (CO₂) desaturation. Model predictions for uniform density foams have been computed and presented for fresh polyurethane foam samples. The transient pressure profiles shown in Figure 1 are computed partial pressure profiles of the blowing agent in uniform density foams, segmented into 10 position fractions along the diffusion path. Figure 1 represents the numerically predicted change with diffusion time of the partial pressure profiles of a blowing agent (CO₂) in a uniform density polyurethane foam with 7 mm thickness. The curves describe the transient local partial pressures of CO₂ in a foam initially saturated at 1.0 atm, which also contained 1.0 atm of air. The depletion of the blowing agent starts at the edges and moves towards the center. With increased age (diffusion time), CO₂ diffuses from the foam and is completely depleted leaving only the original air in the foam. Predicted partial pressure values are tabulated in Tables 1 and 2.

The continuous curves shown in Figure 1, which represent the partial pressures of the blowing agent (CO₂), were computed using the standard analytical solution to the diffusion equation for a constant diffusion coefficient (1.414E-6 cm²/s) using the Fourier series solution. The symbols represent the solution of the implicit (tri-diagonal matrix) form of the differential equation. The transient local component pressures are the same for the standard analytical and implicit (matrix) solutions when using a constant diffusion coefficient. The comparison is presented to demonstrate that the standard Fourier series solution and implicit solution are equivalent when the same constant diffusion coefficient value is used. The results from the numerical solution match within 1% of the values computed from the analytical solution.

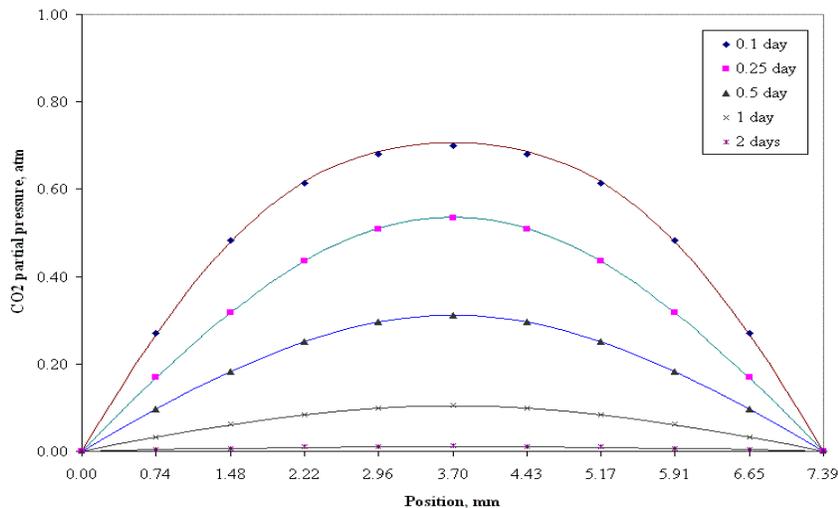


Figure 1. Predicted Transient Partial Pressure Profiles of CO₂ in a Uniform Density Polyurethane Foam

Table 1. CO₂ Partial Pressures of Uniform Density Polyurethane Foam using Tri-diagonal Matrix Method

Position, mm	CO ₂ Partial Pressure, atm				
	2.4 hours	6 hours	12 hours	One day	2 days
0.00	0.00030	0.00030	0.00030	0.00030	0.00030
0.74	0.27009	0.16863	0.09632	0.03247	0.00391
1.48	0.48188	0.31864	0.18292	0.06150	0.00717
2.22	0.61434	0.43535	0.25162	0.08453	0.00976
2.96	0.67977	0.50878	0.29571	0.09932	0.01142
3.70	0.69861	0.53376	0.31090	0.10441	0.01200
4.43	0.67977	0.50878	0.29571	0.09932	0.01142
5.17	0.61434	0.43535	0.25162	0.08453	0.00976
5.91	0.48188	0.31864	0.18292	0.06150	0.00717
6.65	0.27009	0.16863	0.09632	0.03247	0.00391
7.39	0.00030	0.00030	0.00030	0.00030	0.00030

Table 2. CO₂ Partial Pressures of Uniform Density Polyurethane Foam using Fourier Series Solution

Position, mm	CO ₂ Partial Pressure, atm				
	2.4 hours	6 hours	12 hours	One day	2 days
0.00	0.00030	0.00030	0.00030	0.00030	0.00030
0.74	0.26675	0.16814	0.09611	0.03218	0.00383
1.48	0.48047	0.31827	0.18253	0.06093	0.00701
2.22	0.61760	0.43575	0.25110	0.08375	0.00954
2.96	0.68612	0.51011	0.29512	0.09840	0.01116
3.70	0.70581	0.53551	0.31028	0.10345	0.01172
4.43	0.68612	0.51011	0.29512	0.09840	0.01116
5.17	0.61760	0.43575	0.25110	0.08375	0.00954
5.91	0.48048	0.31827	0.18253	0.06093	0.00701
6.65	0.26675	0.16814	0.09611	0.03218	0.00383
7.39	0.00030	0.00030	0.00030	0.00030	0.00030

Air components saturation. Typically a foam, when produced does not contain either nitrogen or oxygen. Figures 2 and 3 represent the computed partial pressure profiles of air components nitrogen and oxygen with diffusion time in a uniform density polyurethane foam using the implicit solution. Both nitrogen and oxygen diffuse inwardly relatively slowly starting at the edges moving toward the center, with time. Since the diffusion coefficients of both nitrogen and oxygen are small compared to that of carbon dioxide, the inward rates of diffusion of the air components are slower than the outward diffusion of carbon dioxide.

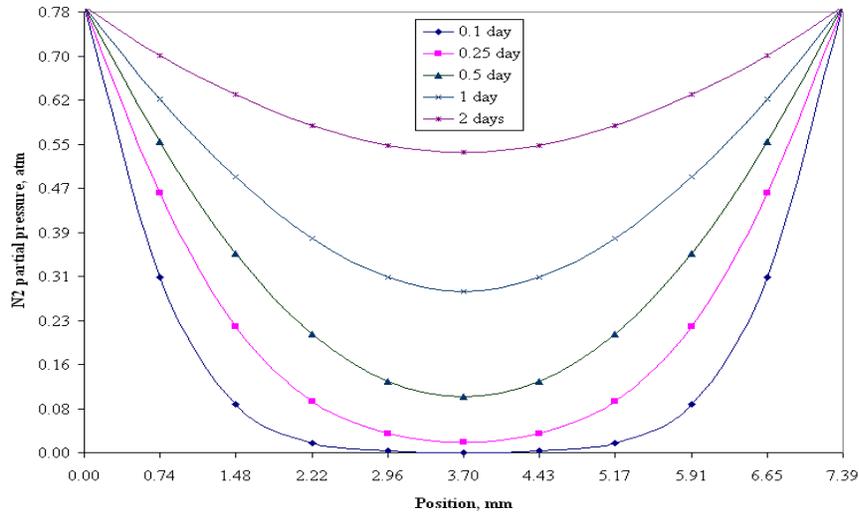


Figure 2. Predicted Transient Partial Pressure Profiles of N2 in a Uniform Density Polyurethane Foam

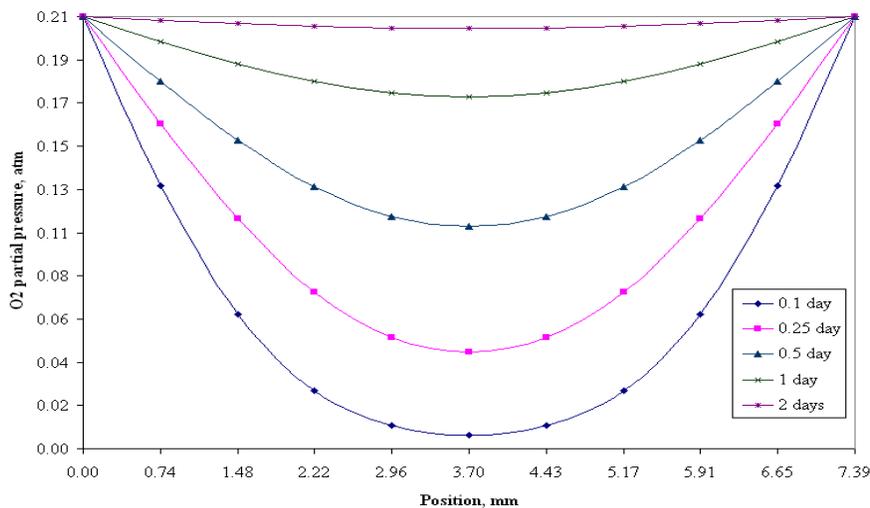


Figure 3. Predicted Transient Partial Pressure Profiles of O2 in a Uniform Density Polyurethane Foam

Predicted Transient Total Pressure Profiles

The transient pressure profiles shown in Figure 4 are total cell gas pressures in a uniform density polyurethane foam computed by the implicit model. The curves show the total pressure profile changes as CO₂ diffuses outward at the same time that the air components are diffusing inward. Together these components produce a variation in the total cell gas pressure with position and time. Because of the high diffusion rate of CO₂, a subatmospheric pressure zone is created, starting at the outside edges, moving toward the center, until the air influx becomes significant.

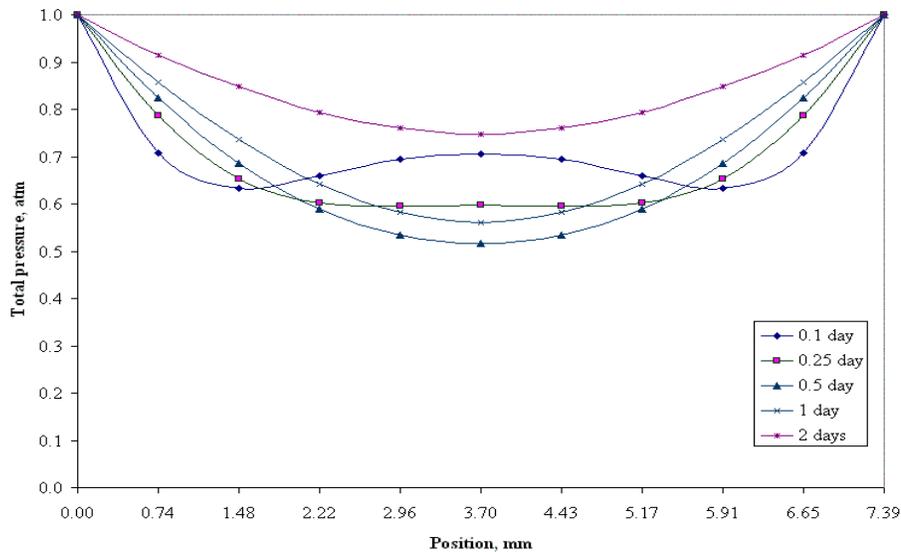


Figure 4. Predicted Transient Total Pressure Profiles in a Uniform Density Polyurethane Foam

At low ambient temperatures (for volatile blowing agents) the vapor pressure of the blowing agent may not be sufficient to provide needed cell gas pressure before the atmospheric gases can diffuse into the core region of the foam. The local cell gas pressure can drop below a stable condition and cellular structure collapse occurs. If only a single component is diffusing in or out of the foam, the pressure gradient is monotonic and the local total pressure profile is gradual. However, when components diffuse in opposite directions, the total pressure gradient may produce a trough or a ridge, which provides an opportunity for a large pressure gradient and may result in cellular damage, depending on the strength of the polymeric cell structure.

Non-uniform Foam Density Distribution

Predicted Transient Partial Pressure Profiles by Implicit Method

Blowing agent (CO₂) desaturation from expanded XPS foam at isothermal conditions. The transient pressure profiles shown are the partial pressure profiles of the blowing agent (CO₂) in a 20mm thick polystyrene foam of variable density, at room

temperature, having an average density of 21 kg/cu.m, segmented into 10 positions along the diffusion path. The density data were used to regress a quadratic equation for the density of the foam. Pressure profiles were computed for quadratic variation of density in the foam. Figure 5 represents the change of the partial pressure profiles of the blowing agent, CO₂ with diffusion time. The values are tabulated in Table 3, which describes the local partial pressure profile of CO₂ in the foam having an initial 1.0 atm partial pressure, placed in an oxygen/nitrogen atmosphere at room temperature. Figure 5 shows the depletion of blowing agent, starting at the edges and moving towards the center with diffusion time. With increased age, blowing agent diffuses from the foam and is completely depleted. There is a variation in the partial pressure values due to density gradient but is nearly same on each side of the foam across the plane but different from uniform density partial pressure values.

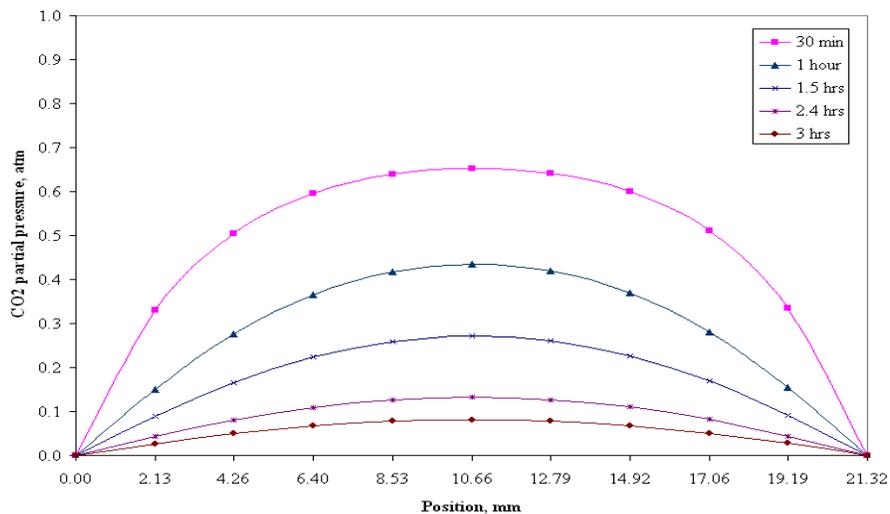


Figure 5. Predicted Partial Pressures of CO₂ in a Variable Density Polystyrene Foam

Blowing agent (CO₂) desaturation from expanded XPS foam at non-isothermal conditions. The transient pressure profiles shown are the partial pressure profiles of the blowing agent (CO₂) in a 20 mm thick polystyrene foam of variable density, having an average density of 21 kg/m³, segmented into 10 position fractions along the diffusion path. The foam has a temperature difference of 10 °C across the foam sample. Pressure profiles are computed for quadratic variation of density and for the temperature gradient across the foam. Figure 6 represent the change with diffusion time of the partial pressure profiles of the blowing agent, CO₂ with diffusion time. The values are tabulated in Table 4. Table 4 describes the local partial pressure profile of CO₂ in the foam having an initial 1.0 atm partial pressure, placed in an oxygen/nitrogen atmosphere with 29 °C (bottom) and 19 °C (top) temperature on the two surfaces respectively. Figure 6 clearly shows the depletion of blowing agent, starting at the edges and moving towards the center. With increased age, blowing agent diffuses from the foam and is completely depleted. Although the density profile is symmetrical about the centerline, the partial pressure values are not symmetrical across the plane because of the additional variation of the diffusion coefficient due to the local linear temperature effect on the diffusion coefficient. The diffusion increases as the temperature increases and the diffusion further increases as the density decreases. From

Table 4, it is shown that the concentration is higher at the topside of the foam sample where the temperature is lower. As the temperature increases across the foam sample to bottom side, the concentration increases across the vertical position of the foam sample, the result of less diffusion.

Table 3. CO₂ Partial Pressures of Variable Density Polystyrene Foam using Tri-diagonal Matrix Method at Isothermal Conditions

Position, mm	CO ₂ Partial Pressure, atm				
	30 min	1 hour	1.5 hours	2.4 hours	3 hours
0.00	0.00030	0.00030	0.00030	0.00030	0.00030
2.13	0.32983	0.15089	0.08954	0.04317	0.02669
4.26	0.50457	0.27514	0.16602	0.08010	0.04943
6.40	0.59583	0.36453	0.22373	0.10817	0.06672
8.53	0.63955	0.41748	0.25931	0.12560	0.07746
10.66	0.65285	0.43544	0.27165	0.13167	0.08120
12.79	0.64182	0.42062	0.26148	0.12668	0.07813
14.92	0.59994	0.36941	0.22702	0.10980	0.06773
17.06	0.50998	0.28010	0.16921	0.08167	0.05040
19.19	0.33493	0.15411	0.09151	0.04414	0.02730
21.32	0.00030	0.00030	0.00030	0.00030	0.00030

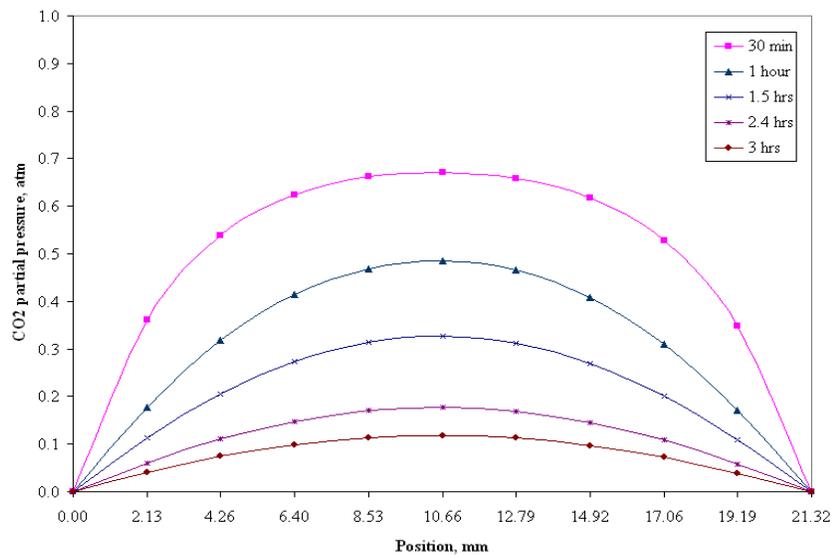


Figure 6. Predicted Non-Isothermal Partial Pressures of CO₂ in a Variable Density Polystyrene Foam

Table 4. CO₂ Partial Pressures of Variable Density Polystyrene Foam using Tri-diagonal Matrix Method for Non-Isothermal Conditions

Position, mm	CO ₂ Partial Pressure, atm				
	30 min	1 hour	1.5 hours	2.4 hours	3 hours
0.00	0.00030	0.00030	0.00030	0.00030	0.00030
2.13	0.36214	0.17754	0.11239	0.06039	0.04018
4.26	0.53818	0.31819	0.20609	0.11105	0.07382
6.40	0.62347	0.41467	0.27449	0.14850	0.09870
8.53	0.66151	0.46862	0.31470	0.17077	0.11352
10.66	0.67134	0.48422	0.32671	0.17750	0.11801
12.79	0.65914	0.46532	0.31246	0.16963	0.11279
14.92	0.61750	0.40771	0.26992	0.14618	0.09720
17.06	0.52764	0.30906	0.20047	0.10823	0.07198
19.19	0.34917	0.17021	0.10820	0.05830	0.03882
21.32	0.00030	0.00030	0.00030	0.00030	0.00030

CONCLUSIONS

A new approach of predicting transient local partial pressures of air components and blowing agent, using an implicit numerical method has been developed. The results were compared to those obtained analytically to demonstrate that the implicit method produces equivalent predicted results for a polymeric foam having a uniform bulk density. The predicted numerical results match within 1% of the analytical values.

The new method of calculation was applied to the desorption and thermal conductivity predictions and demonstrated that regions of variable density can accentuate the total pressure profiles compared with foams of uniform density. Blowing agent transient pressure profiles were predicted using the Tri-diagonal matrix method for variable density XPS foams with isothermal and non-isothermal conditions. Predicted results indicate that the influence of temperature is greater than the effect of variation in density on diffusion coefficients and the resulting pressure profiles.

The effect of transient internal cell gas pressure on the yield strength of cellular plastic foam was briefly evaluated. The surface foam structure may be damaged when the local internal cell-gas pressure becomes significantly below or above a critical value as a result of counter diffusion of gases with widely different diffusion coefficients. A sub-atmospheric or hyper-atmospheric zone in the total cell gas pressure can damage the foam cellular structure.

NOMENCLATURE

c	= volatile solute concentration, gmol/cm ³
D	= diffusion coefficient, cm ² /s
x	= diffusion distance, cm
t	= diffusion time, sec
l	= foam thickness, cm

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