Sample Size Effect on the Effective Diffusion Coefficients for the Gas Contained in Closed-Cell Polyethylene-Based Foam Subjected to Compressive Creep Tests

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ABSTRACT: In this article, the effect of sample size on the degassing behavior of closed-cell low density polyethylene (LDPE) foam under long-term compressive static loading is presented. The creep response was modeled by assuming isothermal compression of the gas. The change in gas pressure with time was obtained and the effective diffusion coefficients were calculated from pressure decrease using an analytical solution of the diffusion equation, and were found to increase when the sample size was reduced. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2204–2210, 2006

Key words: polyethylene foams; diffusion coefficient; creep testing

INTRODUCTION

Closed-cell foams consist of gas bubbles separated by a thin membrane of a continuous macromolecular phase that can be rigid or flexible.[1–3] In several applications, like structural or packaging, foams are frequently loaded for long periods of time, resulting in a time-dependent sample deformation that can seriously affect its properties. When closed-cell foams are compressed, the continuous deformation is caused by the polymer matrix creep and by the slowly outward diffusion of the gas contained in the cells.[4] On the other hand, it is well established that gas diffusion, often called ageing, affects the thermal insulation capability and dimensional stability of foams.[5,6] Hence, understanding and modeling the gas diffusion process in closed-cell foams is of great importance from both fundamental and practical viewpoints.[1]

In the previous investigations, the prediction of gas diffusion through closed-cell foams is accomplished via two different types of models that use either discrete or continuous approaches. The continuous diffusion models consider the foams as an homogeneous and isotropic medium through which a gas species "i" diffuses with an effective diffusion coefficient $D_{\text{eff},i}$.[1] The composition of each species in the foam is found from the analytical solution of the diffusion equation:[7–9]

$$\frac{\partial P_i}{\partial t} = D_{\text{eff},i} \nabla^2 P_i \tag{1}$$

where P_i is the partial pressure of gas i and $D_{\text{eff},i}$ is the effective diffusion coefficient of the foam. A major disadvantage of continuous models is that they give no physical insight into the effect of foam geometrical structure on the diffusion process.

The discrete diffusion models consider the foam as the repetition of unit cells characterized by their wall thickness, cell size, and shape, as well as the diffusivity of the gas species through the polymeric matrix and through the gas phase. Most of these models use an electrical network analogy to represent diffusion through the foam.[6,7]

The discrete models are also based on the assumptions that if the material is mainly amorphous, for steady state conditions, the Henry's law is applicable so the permeability coefficient for gas i through the membrane (P_i) can be expressed as follows:[1]

$$P_i = D_i S_i \tag{2}$$

where D_i and S_i are the diffusion coefficient and the solubility of the gas i in the membrane (Henry's law and steady state conditions are hardly satisfied in the practice[1,7]).

The diffusion coefficient of the gas i in the polymeric matrix depends on the physical and chemical charac-

teristics of the polymer. Besides, for closed-cell foams, it is expected that as the face cell becomes thinner, the diffusion resistance decreases, leading to larger diffusion coefficients.[4,6] In addition, temperature has a significant influence on the diffusion. Gas diffusion through the solid phase is considered to be a thermally activated process[1] in which the temperature dependence is given by

$$D_i = D_0 \exp\left(-\frac{E_i}{RT}\right) \qquad (3)$$

where D_i is the gas diffusion coefficient of gas species i through the solid phase, and D_0 and E_i are experimentally determined constants.

Summarizing the literature review, it seems that it is well established that the effective diffusion coefficient value of a gas species i in a foam depends on foam morphology parameters (wall thickness, cell size and shape, foam density, etc), on the diffusion coefficients in the gas and solid phases and on the temperature.[1,6,7]

However an additional parameter, which might influence the gas diffusion, is sample size. Moreover, as far as we know, no set of data is available in the literature, but only marginal comments about the effect of sample size on the degassing behavior of closed-cell foams subjected to compressive static loading. In the model developed by Pilon et al.[1] it is assumed that there exists some dependency between effective diffusion coefficient and sample size:

$$(D_{\text{eff},i})_{\text{foam}} = \left(\frac{\phi}{L_f}\right) D_{\text{eff},i} \qquad (4)$$

where $D_{\text{eff},i}$ is the effective diffusion coefficient of the gas i through the unit cell, Φ is the unit cell size, and L_f is the foam thickness. As the number of cells increases in the diffusion direction, the resistance to the gas diffusion increases, which is a sample size dependency.

Briscoe et al.[10] mention that the inward diffusion of oxygen through crosslinked low density polyethylene (LDPE)-based semifoam is dependent upon the geometry and size of the sample, so a smaller sample size will present larger diffusion coefficients.

Taking into account the previous idea, the aim of this study is to report new experimental data for single closed-cell XLDPE-based foam for the sample size effect on the effective diffusion coefficients values of a closed-cell foam when loaded in compression.

MATERIALS

The main foam characteristics are summarized in Table I. The studied foam was produced by a two stage press

TABLE I
Main Characteristics for the Foam Studied

	Pe20N cross-linked LDPE
Density, ρ_f	40.45 ± 1.53 (kg/m^3)
Average cell size, ϕ	212.1 ± 9.0 (μm)
Face thickness, δ	1.55 ± 0.1 (μm)
Crystallinity, χ	39.1 ± 0.96 (%)
Melting temperature, T_m	109.7 ± 0.32 (°C)

molding procedure,[11,12] using azodicarbonamide and dicumyl peroxide as foaming and crosslinking agents. The material presented an average density of 40 kg/m^3 and a $(5 \pm 0.5)\%$ carbon black content as determined by thermogravimetric measurements, and was based on a LDPE resin. The melting point and crystallinity[13] of this foam were 109.7°C and 39%, respectively. These values were measured by differential scanning calorimetry. By using scanning electron microscopy, the mean cell size and cell wall thickness were also obtained (the experimental method has been published eslsewere[14,15]). The foam was a closed-cell material with cells that in average had a diameter of 212 μm.

Creep experiments

The standard creep test measures the dimensional changes that occur during time under a constant static loading.[16] A home-designed compressive creep apparatus[17] was used to measure the response of the foams to an applied constant stress over a 7 days period at room temperature. Two creep rigs are shown in Figure 1. In each of them, the thickness of the foam is monitored with a linear variable displacement transducer (LVDT) that is connected to a computer. The accuracy of the LVDT was 0.1 μm.

The sample sizes were $50 \times 50 \times 50$ mm^3, $40 \times 40 \times 40$ mm^3, $30 \times 30 \times 30$ mm^3, and $20 \times 20 \times 20$ mm^3. One of the main parameters to be considered in the diffusion mechanism is the ratio between the sample volume and the sample surface. In this investigation, the shape of the samples (cubic) was fixed changing the surface to volume ratio.

For each sample size, experiments at 4 different stresses (99.2, 76.9, 65.8, and 59.2 kPa) were carried out.

RESULTS

The response in the compressive creep tests is an instantaneous strain that depends upon load applied, followed by a minor strain increase as a function of creep time (Fig. 2).

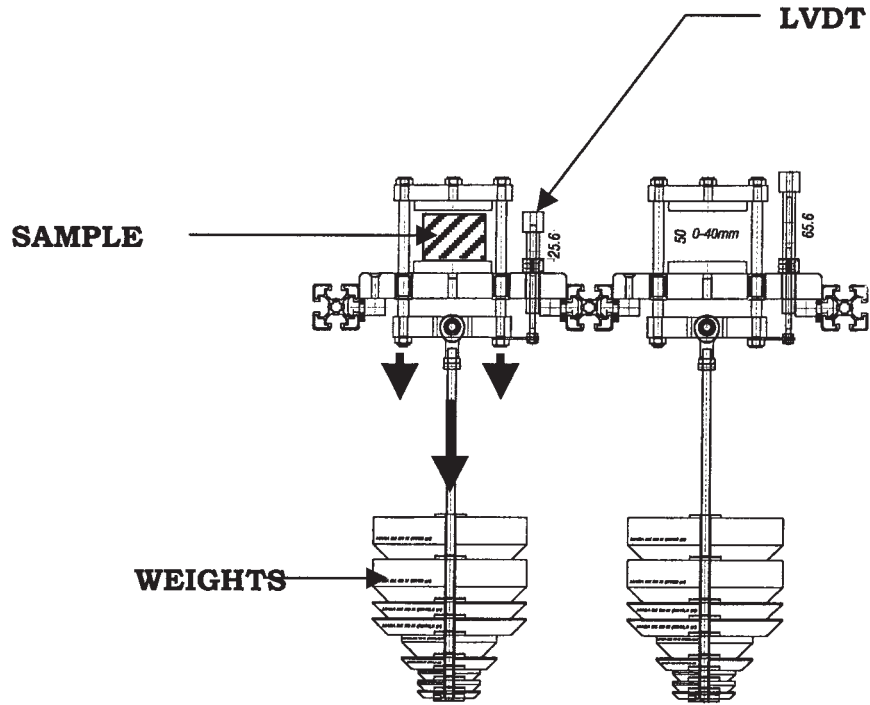When closed-cell foams are loaded in the postcollapse region, assuming the isothermal compression of

Figure 1 Two compressive creep rigs.

the gas and nonlateral expansion, the compressive stress (σ) can be obtained from the following equation:[2,18,19]

$$\sigma = \sigma_0 + \frac{P_o \varepsilon}{1 - \varepsilon - \rho_f/\rho_s} \qquad (5)$$

where σ_0 is the initial polymer yield stress, ε is the strain, P_0 the initial pressure inside the cells, and $R = \rho_f/\rho_s$ represents the relative density, i.e., the foam density divided by the solid polymer density. The term $\varepsilon/(1 - \varepsilon - R)$ is called "gas volumetric strain"
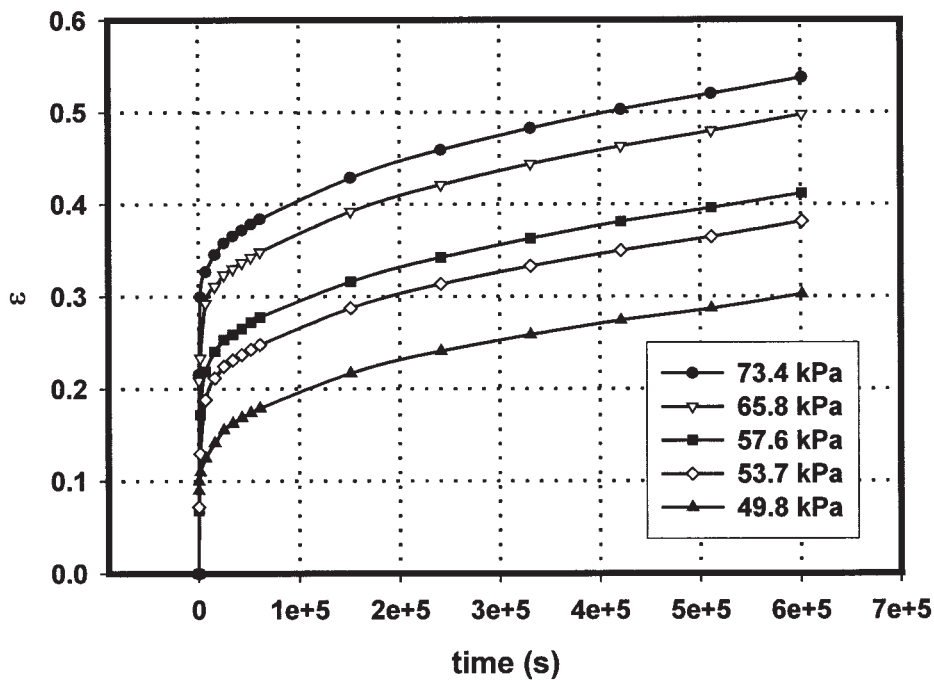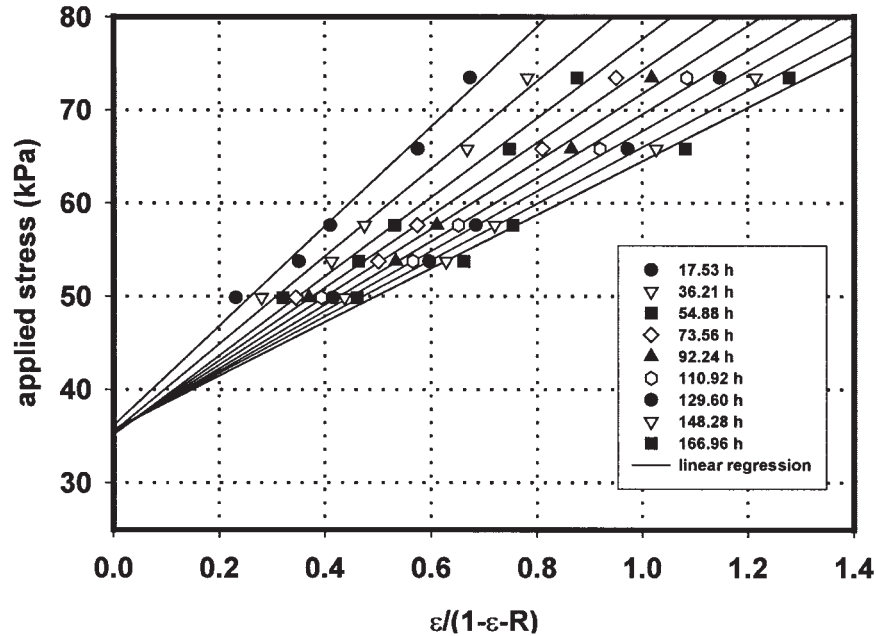

Figure 2 Characteristic creep response of Pe20N foam sample ($50 \times 50 \times 50$ mm^3) at five different applied stresses.

Figure 3 Typical isochronous (applied stress) *versus* (gas volumetric strain) curves for a Pe20N foam of $50 \times 50 \times 50$ mm^3 sample size.

and represents the contribution of the gas to the foam compressive response.

Isochronous stress versus gas volumetric strain curves were obtained from the experimental data, for all the sample sizes, plotting the compressive stress applied as a function of $\varepsilon/(1 - \varepsilon - R)$ for a fixed creep time. The slope of these curves represents, in this isothermal compression model, the pressure of the gas contained in the cells (Fig. 3).

The slope of the isochronous stress versus gas volumetric strain curves decreases with creep time, therefore the pressure inside the cells decreases with time.

The effective diffusion coefficients values can be obtained from the evolution of pressure with time using a solution of the diffusion equation proposed by Svanström et al.[20] and valid for foam slabs.

$$D_{\text{eff}} = -\frac{L^2}{\pi^2} \frac{\{\ln[(P_{\text{total}}\pi^2)/(8P^0)]\}}{dt} \qquad (6)$$

where L is the thickness of the slab, P_{total} is the pressure inside the cells at a time t, and P_0 is the pressure in the cells for the unloaded foam.

To obtain the values of the initial pressure inside the undeformed foam, the values of pressure were fitted to an exponential decreasing function.

From Figure 4, where the relative pressure values after the creep period, i.e., the pressure after the creep period divided by initial pressure, are presented, as a function of sample size (sample edge length), it is clear that the smaller samples degasses at higher rates for the same stress conditions.

Typical curves for $(P^2\pi/P^0)$ are shown in Figure 5. These curves were fitted to linear ones. Their slopes are closely related to effective diffusion coefficients. In Figures 6 and 7 the values obtained for D_{eff} are plotted as a function of sample edge and the ratio between sample volume and area respectively.

The data represented in Figure 7 were fitted with a good accuracy to the empirical equation:

$$D_{\text{eff}} = \frac{a}{1 + e^{\frac{-(x-x_0)}{b}}} \qquad (7)$$

where x stands for the ratio of sample volume to total area and the fitting constants are $a = 2.54 \times 10^{-10}$ m^2/s, $b = 1.47 \times 10^{-3}$, and $x_0 = 7.72 \times 10^{-3}$.

DISCUSSION

The values obtained in our study for the effective diffusion coefficients were approximately of the same order of magnitude than those found in literature The values for these parameters corresponding to gas contained in the cells for crosslinked LDPE (densities 66 and 22 kg/m^3) foams have been predicted theoretically by Mills and Gillchrist[4] (using a discrete model for the undeformed foam) and were reported: D_{eff} (LDPE, $\rho_f = 66$ kg/m^3)~250×10^{-12} m^2/s and D_{eff} (LDPE, $\rho_f = 22$ kg/m^3)~500×10^{-12} m^2/s. High density crosslinked LDPE-based semifoams were studied during storage[10] by Briscoe, obtaining effective coefficient values varying between 10^{-10} and 10^{-11} m^2/s
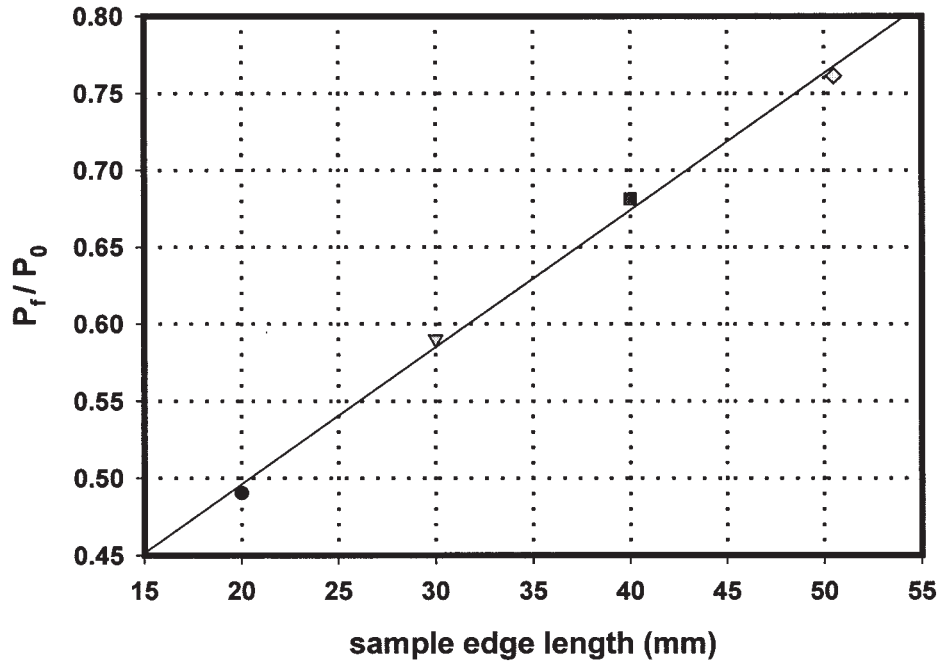
Figure 4 Curves for the relative pressure decrease (final pressure divided by initial pressure) as a function of sample size (sample edge length).

depending on the matrix volume fraction (relative density).

The values obtained for D_{eff} depend upon sample size in agreement with the qualitative predictions of Pilon[1] and Briscoe[10] and smaller sample sizes present larger diffusion coefficients. In fact, Pilon et al.[1] reported that their experiments suggest the effective diffusion coefficient through foams can be expressed
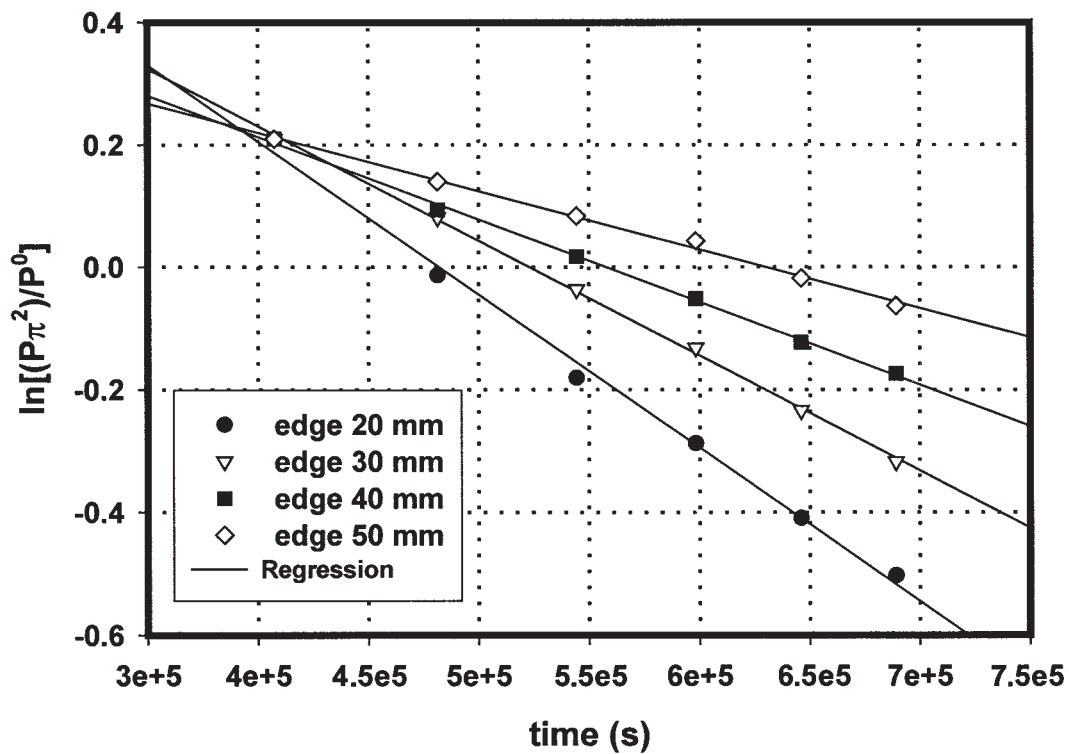

Figure 5 Curves for the logarithmic relative pressure decrease as a function of time.
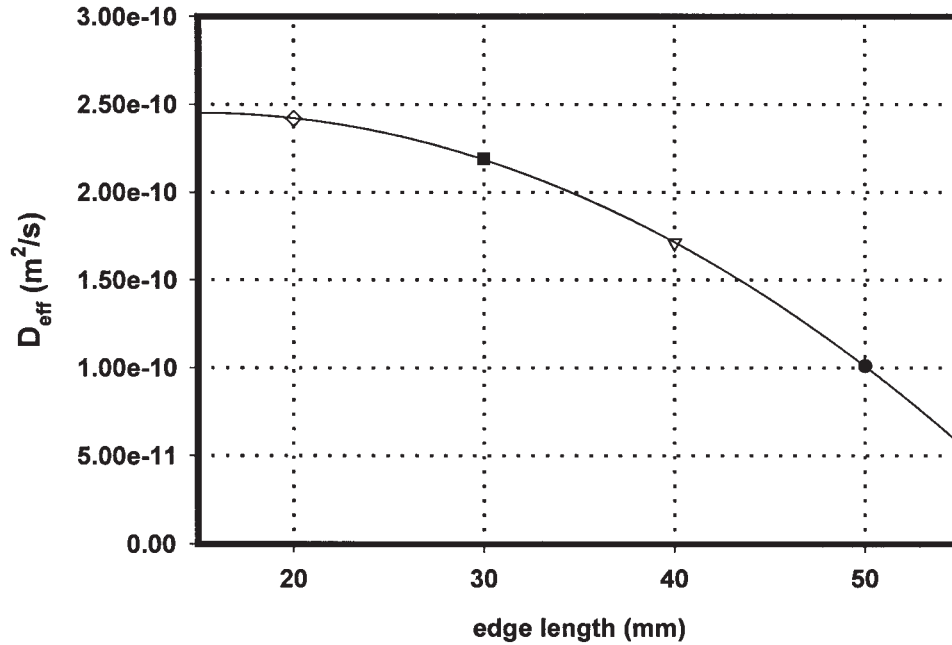
Figure 6 Effective diffusion coefficient values as a function of sample size.

as a product of a sample geometrical factor and the gas diffusion coefficient through the membrane.

Data for D_{eff} and number of cells (n) corresponding to the sample sizes under study are presented in Table II. As the average number of cells increases, the diffu-sion coefficients decrease. For the foam-studied D_{eff} values were fitted to a second order function in n

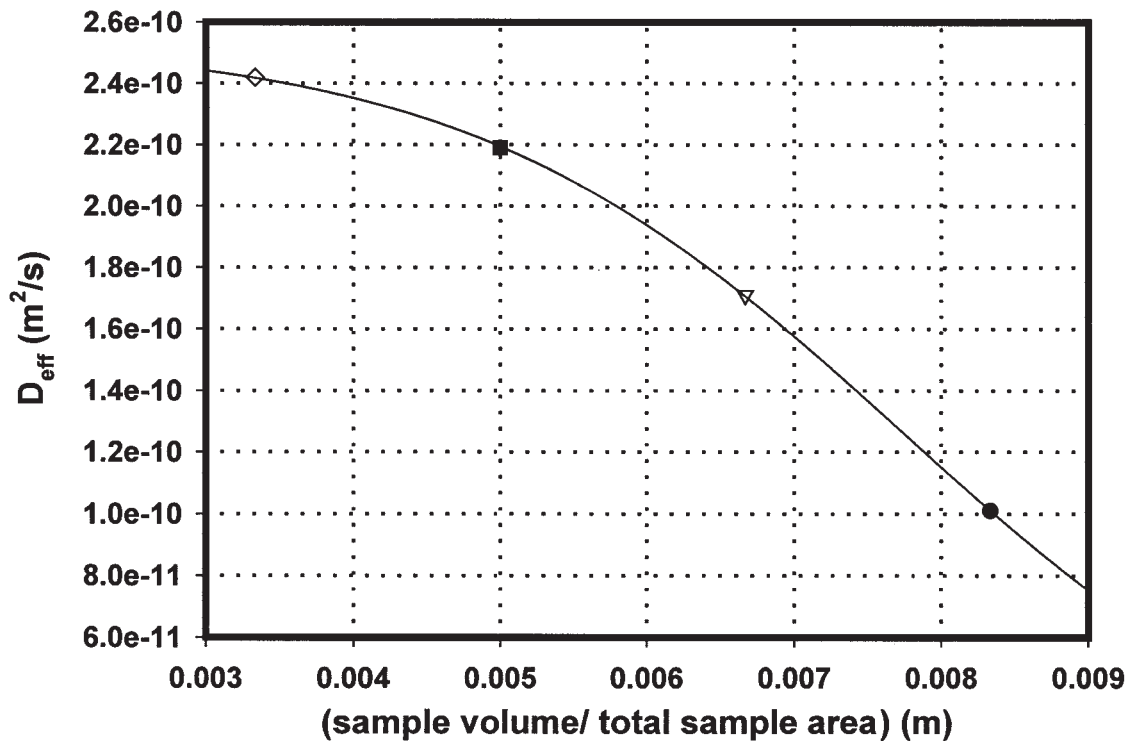$$D_{eff} = 2.18 \times 10^{-10} + 7.45 \times 10^{-13}n - 5.28 \times 10^{-15}n^2$$

Figure 7 Effective diffusion coefficient values as a function of the relationship between sample volume and area.

TABLE II
Average Number Cells, Effective Diffusion Coefficients Values and Sample Edge Length for the Foams Studied

L_f/ϕ (cells number)	D_{eff} (m²/s)	Sample edge (m)
235.8	1.01×10^{-10}	0.050
188.6	1.71×10^{-10}	0.040
141.5	2.91×10^{-10}	0.030
94.3	2.42×10^{-10}	0.020

Bart et al.,[6] in a more general way, proposed another geometrical factor F_{geom} (the same for all gases within the foam) depending on geometrical foam characteristics (cell elongation, orientation, size, etc.), which relates foam effective diffusion coefficient to polymer diffusivity, and could be, in the case of anisotropic inhomogeneous foam, a position dependent tensor.

Moreover, when a foam is produced by the molding procedure (which maintains the foam block exterior at relative constant temperature), due to the heat generated by the decomposition of blowing agent, and to the low thermal conductivity of the polymeric matrix, the interior of the foam will be at higher temperature than that in the boundaries. This produces bigger cell volume in the central part of the foam surface and due to lower viscosity, thinner cell faces. Then it is expected for effective diffusion coefficients to be larger in the central part of the foam block than at its boundaries.[6] Moreover, the foam effective diffusion coefficient (D_{eff}) is not only determined by the geometrical characteristics of the foam structure but also mainly by the chemical and physical structure of polymer matrix. These features could be affected by the different thermal history due to different temperature gradients.

Though care has been taken in the election of the samples so that they correspond to the same block foam zone, the above factors may affect the predictions about the diffusivity size dependence and lead to different dependencies between D_{eff} and the average cell number (n).

It would be very interesting to study the diffusion size dependence in the case of nitrogen solution process that produces highly isotropic foams but with the drawback of limited sample thickness available.

CONCLUSIONS

An experimental study of the sample size dependence degassing behavior of LDPE foam subjected to compressive loading has been presented. Comparison of data available in the literature for effective diffusion coefficient values of LDPE foams shows qualitative agreement. For cubic samples, the tendency of the effective diffusion coefficients is to decrease when the ratio of sample volume to total area increases. So the values obtained for D_{eff} depend upon sample size in agreement with previous predictions and smaller sample sizes present larger diffusion coefficients.

As the average number cells across the foam in the direction of flux increase, the diffusion coefficients decrease and for the foam studied, D_{eff} were fitted to a second order function in n. Further study in the case of highly isotropic foams would be very interesting.

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