
Gas Diffusion in Polyolefin Foams During Creep Tests. Effect on Impact Behaviour and Recovery after Creep

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ABSTRACT

A method to obtain the effective diffusion coefficient of the gas contained in closed cell polyolefin foams under static loading is presented. This property is obtained from pressure decrease with time using an analytical solution of the diffusion equation. The effect of density, type of base polymer, crosslinking and sample size on the diffusion coefficient is analysed.

It has been shown that the impact behaviour of low density closed cell polyethylene based foams deteriorates after compressive creep periods and that this reduction of the cushion capabilities is directly related with the diffusion coefficient of the foams.

Moreover, the recovery of the foams after creep showed a peculiar non-homogeneous behaviour, which has been analysed. Gas diffusion during creep is the main responsible for this particular behaviour.

1. INTRODUCTION

Closed cell polymeric foams have a wide range of applications in which its unique combination of properties is exploited⁽¹⁾. In some of these applications such as cushioning and packaging, the foams are subjected to static loads which can be long enough to produce a significant foam deformation. Under these conditions, the mechanical properties are affected due to, on the one hand, the plastic deformation of the polymeric matrix and on the other hand, to the gas

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diffusion from the cells⁽²⁾. Due to this reason, understanding and modelling the creep response and the closely related degassing behaviour under static loads is an important issue from both fundamental and practical viewpoints⁽³⁾.

There have been some attempts to relate the creep behaviour of cellular solids to their cellular structure and base material properties. Several authors have proposed⁽⁴⁻⁶⁾ modelling the foam creep response in terms of the creep behaviour of the matrix, predicting a creep rate proportional to $(\rho/\rho_s)^n$ where n is an empirical constant that accounts for the creep behaviour of the polymeric matrix.

However, in flexible closed-cell polymeric foams, loaded in the post-collapse region, there is also a non-negligible contribution of gas escape to the creep response^(7,8). In the literature, the prediction of gas diffusion through closed-cell foams is accomplished via two different types of models, which use either discrete or continuous approaches. The continuous diffusion models consider the foams as an homogeneous and isotropic medium through which gas species “ i ” diffuses with an effective diffusion coefficient $D_{\text{eff},i}$ ⁽³⁾. The composition of each species in the foam is found from the analytical solution of the diffusion equation⁽⁹⁻¹¹⁾:

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

where P_i is the partial pressure of gas- i and $D_{\text{eff},i}$ is the effective diffusion coefficient of the foam for the gas “ i ”. An important 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 a repetition of unit cells characterised by their wall thickness, cell size and shape, as well as the diffusivity of the each gas through the polymeric matrix and through the gas phase. Most of them use an electrical network analogy to represent diffusion through the foam^(9,12).

Briscoe studied experimentally and theoretically the degassing behaviour of LDPE high density foams during storage⁽¹³⁾, obtaining effective diffusion coefficients varying between 10^{-10} and 10^{-11} m²/s depending on the matrix volume fraction (relative density). Mills^(2,7) using a discrete model predicted a diffusion coefficient for the foam given by:

$$D_{eff} = \frac{6Pp_a}{f_f R} \quad (2)$$

where P is the polymer permeability, p_a the initial pressure in the cells, f_f the fraction of polymer in the foam cell faces and R the foam relative density.

In addition, only marginal comments about the effect of sample size on the degassing behaviour of LDPE based closed-cell foams subjected to compressive static loading has been published. In the model developed by Pilon *et al.*⁽³⁾, it is supposed that there exists some dependency between the effective diffusion coefficient and sample size:

$$(D_{eff,i})_{foam} = \left(\frac{\phi}{L_f} \right) D_{eff,i} \quad (3)$$

where $D_{eff,i}$ 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 gas to diffusion increases, which is a sample size dependency.

Briscoe *et al.*⁽¹³⁾ mentioned that the inward diffusion of oxygen through crosslinked LDPE-based semifoam (which is an intermediate stage in the production of the foam) is dependent upon the geometry and size of the sample, so a smaller sample size will present larger diffusion coefficients.

The previous literature review indicates that there has been an interest in this subject. However most of the investigations have used a theoretical approach modelling the foam behaviour. Our goal is to present a simple method based on both creep experimental data and a mathematical solution of the diffusion equation, to obtain reliable data for the effective diffusion coefficients of flexible polymeric closed-cell foams. These results have been used to study, on the one hand, the structure-property relationship for this property and, on the other hand, to show the effect of gas diffusion in the response of the foams after creep and in the foams performance under impact conditions.

2. MATERIALS

The main foam characteristics are summarized in Table 1. Seven of the studied foams were crosslinked materials and were produced by a two-stage press moulding procedure^(14,15). The foam called “NCLDPE” was produced

Table 1. Characteristics for the foams under study: density (ρ_f), average cell size (Φ), face thickness (δ), crystallinity (X_c) and melting point (T_m)

Sample	ρ_f (Kg/m ³)	Φ (μ m)	δ (μ m)	X_c (%)	T_m (°C)
XLDPE15 crosslinked LDPE	59.51 \pm 3.19	162.0 \pm 13.1	2.0 \pm 0.1	34.4 \pm 0.2	108.9 \pm 0.39
XLDPE20 crosslinked LDPE	36.91 \pm 2.11	213.5 \pm 8.8	1.5 \pm 0.1	35.2 \pm 1.36	108.9 \pm 0.44
XLDPE30 crosslinked LDPE	25.46 \pm 1.06	255.2 \pm 8.2	1.2 \pm 0.1	36.7 \pm 0.79	108.8 \pm 0.33
XLDPE40 crosslinked LDPE	23.80 \pm 1.40	263.4 \pm 23.9	1.1 \pm 0.1	30.7 \pm 1.01	108.8 \pm 0.21
XEVA20 crosslinked EVA	43.51 \pm 1.35	214.3 \pm 15.4	1.4 \pm 0.1	22.7 \pm 1.71	86.6 \pm 0.75
XEVA30 crosslinked EVA	28.73 \pm 1.01	246.6 \pm 13.1	1.1 \pm 0.1	22.8 \pm 1.10	88.2 \pm 0.78
XLDPE20N crosslinked LDPE	40.45 \pm 1.53	212.1 \pm 9.0	1.55 \pm 0.1	39.1 \pm 0.96	109.7 \pm 0.32
NCLDPE non-crosslinked LDPE	35.59 \pm 1.40	~2000	-	31.5 \pm 1.15	108.4 \pm 0.56

by means of an extrusion process and do not present a cross-linked base polymer. The EVA foams presented a 19% vinyl acetate content. Finally, the foam called "XLDPE20N" presented a 5 \pm 0.5% carbon black content as determined by thermogravimetric (TGA) measurements.

3. Experimental

The materials were characterised using standard techniques (differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electronic microscopy (SEM)) using experimental methods described elsewhere^(16,17).

Creep tests were carried out using a home-designed compressive creep apparatus⁽¹⁶⁾. The sample size was 40 \times 40 \times 30 mm³ except for the NCLDPE and XLDPE20N foams. For these materials slightly bigger samples 50 \times 50 \times 50 mm³ were used. For each foam, experiments at 5 different stresses were carried out. Temperature was 23 \pm 2 °C. Creep time was seven days.

4. Foams Characterisation

The materials under study were almost isotropic (i.e. cell size was very similar in different directions, Figure 1. The mean cell size for foams is largely dependent upon the manufacturing process⁽¹⁴⁾. As

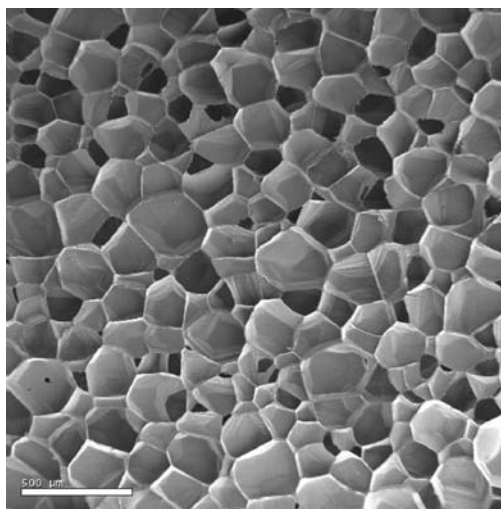


Figure 1. Cellular structure of one of the foams (XLDPE40)

it can be seen in Table 1, for the LDPE crosslinked foams, the face thickness increases with increasing density and the higher the density the lower the mean cell size. These features are characteristic of the two stage press moulding procedure where the density of the foam is mainly controlled by the blowing agent content^(14,15).

The non-crosslinked foam presented much larger (~2 mm) and irregular cells. Due to the extrusion process the cells were slightly elongated in the extrusion direction (mechanical tests were performed perpendicularly to this direction).

The cell size of EVA foams was very similar to that of crosslinked LDPE foams of similar density. As expected, EVA foams presented a smaller melting point and lower crystallinity than LDPE materials. The similar melting temperatures and crystallinities of the crosslinked LDPE foams indicate similar grades of the LDPE used in the manufacturing process of all these foams.

5. METHOD TO DETERMINE THE DIFFUSION COEFFICIENT

The method to determine the diffusion coefficient has three steps:

1. Creep experiments with different static stresses are performed (Figure 2a).

2. For closed-cell foams loaded in the post-collapse region (plateau), assuming an isothermal compression of the gas and non-lateral expansion, the uniaxial compressive stress (σ) can be obtained from the expression^(1,4,18):

$$\sigma = \sigma_0 + \frac{P_0 \varepsilon}{1 - \varepsilon - \rho_f / \rho_s} \quad (4)$$

where σ_0 is the initial polymer yield stress, ε is the deformation, P_0 the initial pressure inside the cells and $R = \rho_f / \rho_s$ the relative density of the foam, i.e. the density of the foam (ρ_f) divided by the density of the solid polymer (ρ_s). The term $\varepsilon(1 - \varepsilon - R)$ is called “gas volumetric strain” and represents the contribution of the gas to the foam compressive response.

Isochronous (stress applied) vs. (gas volumetric strain) (Figure 2b) curves are obtained 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.

3. The effective diffusion coefficients can be obtained from the evolution of pressure with time (Figure 2c) using a solution of the diffusion equation proposed by Svanström *et al.*⁽¹⁹⁾ and valid for foam slabs.

$$D_{\text{eff}} = -\frac{L^2}{\pi^2} \frac{d\left\{\ln\left[\frac{P_{\text{total}} \pi^2}{8P_0}\right]\right\}}{dt} \quad (5)$$

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.

Using this method, values of D_{eff} can be obtained. Figure 3 shows these values for the foams under study in this paper.

6. Diffusion Coefficient as a Function of the Foam Characteristics

The values for the effective diffusion coefficients obtained in this study are of the same order of magnitude (between 2×10^{-10} and 8×10^{-10} m²/s) 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/m³) foams have been predicted theoretically by Mills and Gillchrist⁽⁴⁾ (using a discrete model for the undeformed foam) and were reported to be: D_{eff} (LDPE, $\rho_f = 66$ kg/m³) $\sim 2.5 \times 10^{-10}$ m²/s and D_{eff} (LDPE, $\rho_f = 22$ kg/m³) $\sim 5 \times 10^{-10}$ m²/s. High density crosslinked LDPE-based semifoams were studied during storage by

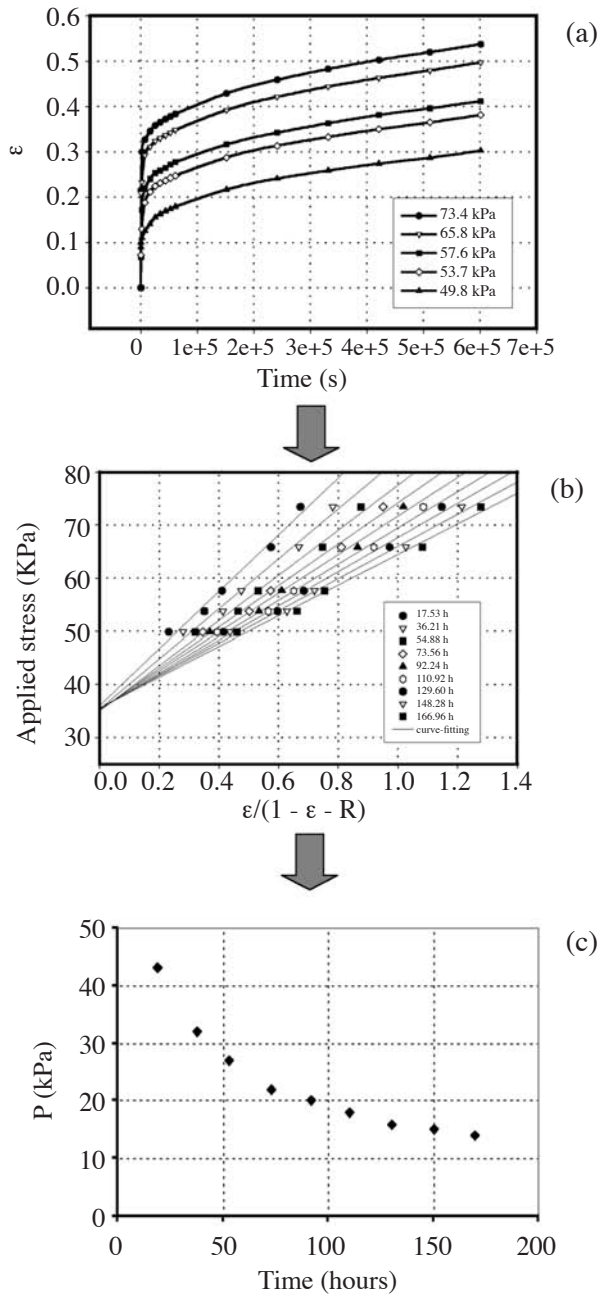


Figure 2. a) Creep response of the XLDPE20N foam at five different applied stresses b) Typical isochronous (applied stress) versus (gas volumetric strain) curves for the XLDPE20N foam, c) Gas pressure as a function of creep time for the XLDPE20 foam

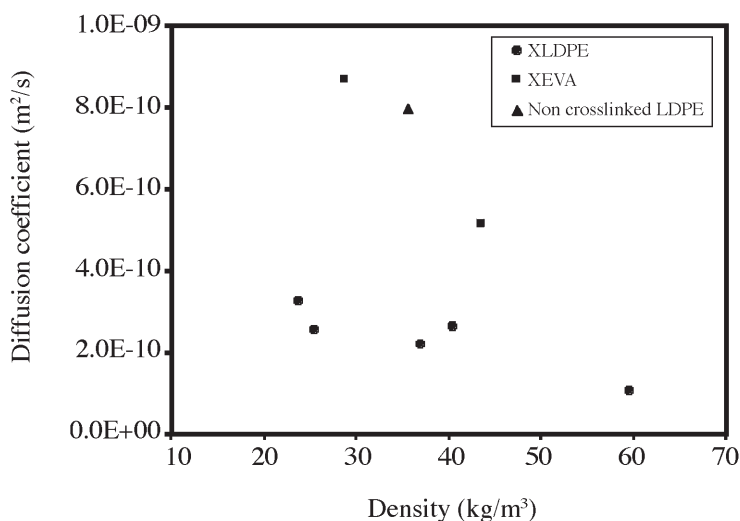


Figure 3. Effective diffusion coefficients as a function of foam density for the foams under study

Briscoe⁽¹³⁾, obtaining effective coefficient values varying between 10^{-10} and 10^{-11} m²/s depending on the matrix volume fraction (relative density).

In addition, the values for the crosslinked LDPE foams with the same sample size, varied inversely with foam density (Figure 4) in agreement with the predictions of Mills equation (equation 2).

The EVA foams presented values for D_{eff} higher than the LDPE ones, which can be understood in terms of its lower crystallinity. The factors involved are the tortuosity of the gas path through the amorphous phase and the effect of the crystals in restricting the mobility of the amorphous polymer chains⁽²⁰⁾.

The non-crosslinked LDPE foam presented values for effective diffusion coefficient much higher than the crosslinked LDPE based ones. This difference probably arises from the different segment mobility in the amorphous phase of the base polymer due to crosslinking.

During the seven days experiments, the pressure was reduced by a factor that depends on density; for example, for the lowest density foam XLDPE40 an 88% reduction of pressure was obtained ($P/P_0 = 0.12$). The reduction in the gas content in the cells can be obtained from pressure decrease through the equation:

$$\frac{n}{n_0} = \frac{P}{P_0} \frac{(1 - \epsilon_{\max}) \rho_s - \rho_f}{\rho_s - \rho_f} \frac{1}{1 - \epsilon_{\max}} \quad (6)$$

where n and n_0 are the gas content inside the cells after and before the creep experiment, ϵ_{\max} is the maximum deformation during the experiment, ρ_f, ρ_s are the densities of foam and solid polymer and P and P_0 are the pressure inside the cells after and before the creep experiment.

Almost all the gas (90% for the XLDPE40 foam at a static stress of 73.3 kPa) has escaped from the foam in a seven days experiment.

In Figures 5 and 6 the values obtained for D_{eff} are plotted as a function of sample edge and the ratio between sample volume and area respectively. The values obtained for D_{eff} depend upon sample size in agreement with the predictions of Pilon⁽³⁾ and Briscoe⁽¹³⁾. Smaller sample sizes present larger diffusion coefficients, being this relationship non-linear. The data represented in Figure 6 can be fitted to the following equation:

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

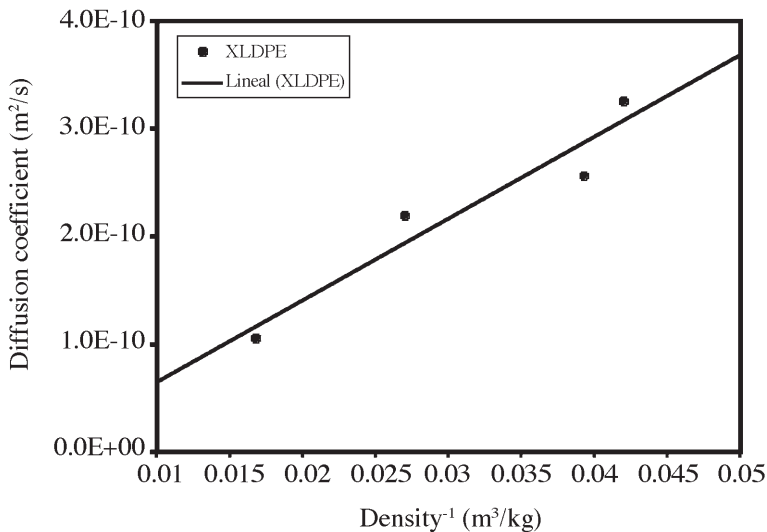


Figure 4. Effective diffusion coefficients for the equal sized crosslinked LDPE foams as a function of $(1/\rho)$

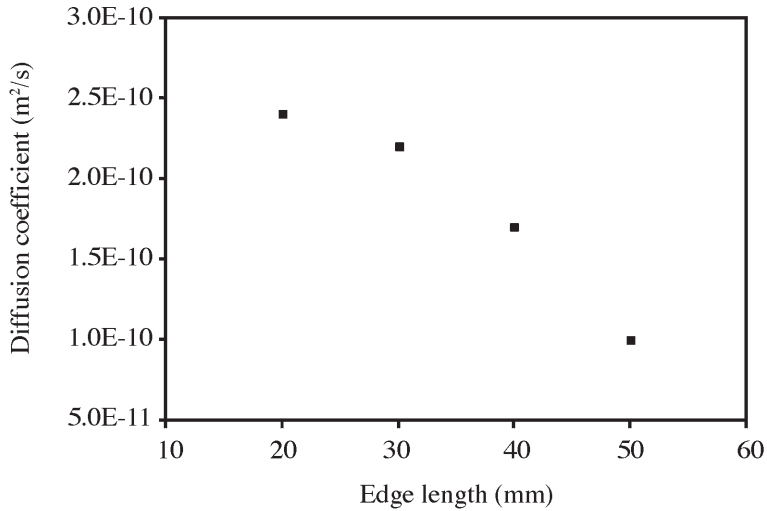


Figure 5. Effective diffusion coefficient values as a function of sample size for crosslinked LDPE foams

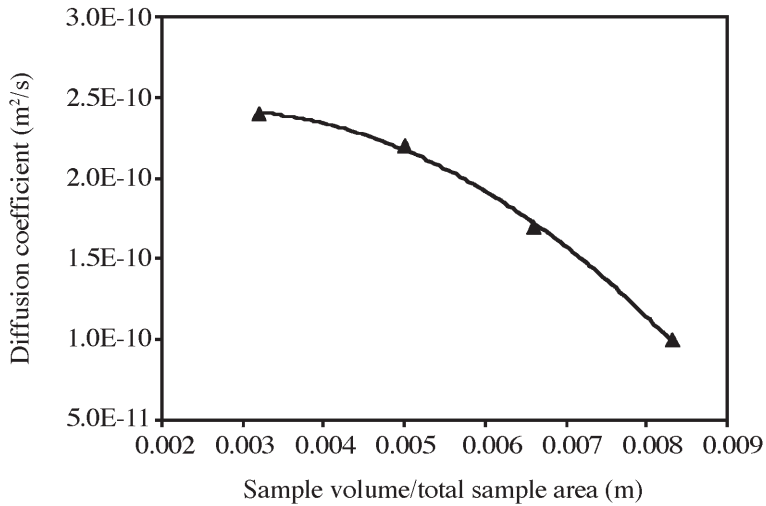


Figure 6. Effective diffusion coefficient values as a function of the relationship between sample volume and area for crosslinked LDPE foams

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

7. IMPACT BEHAVIOUR AFTER COMPRESSIVE CREEP PERIODS

All the studied foams were subjected to a seven days compressive creep period for each compressive creep stress and then were impact tested (with a delay time of three minutes) at the same impact conditions (falling height 0.3 metres and static stress 14 kPa).

The ability to absorb mechanical energy (measured using the deceleration peaks) clearly deteriorates after the compressive creep period for all the studied foams. One typical example is showed in Figure 7.

Moreover, it has been observed that there is a close relationship between the diffusion coefficient D_{eff} and the percentage of deceleration loss due to creep (Figure 8). In this figure, the percentage of deceleration loss was calculated for a creep stress of 40 kPa in experiments of one week. This percentage can reach a value of more than 300% for a low density (36 kg/m^3) non-crosslinked

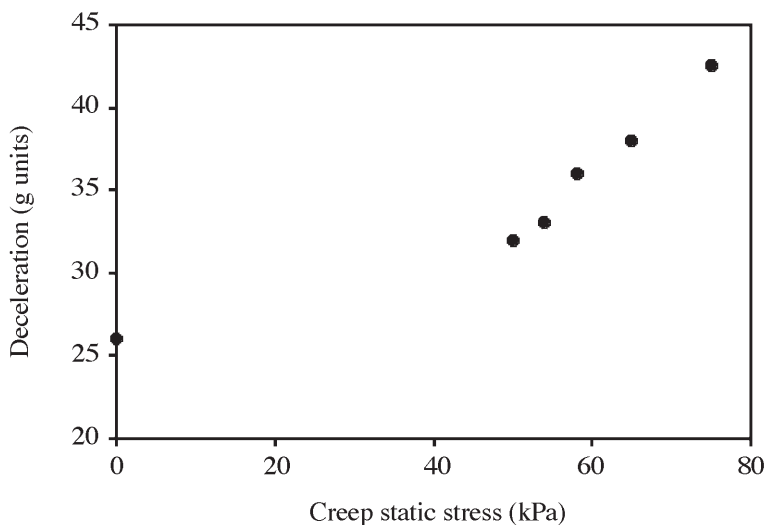


Figure 7. Deceleration peaks for a polyethylene based closed-cell foam XLDPE20N (density 40 kg/m^3) as a function of the compressive creep stress

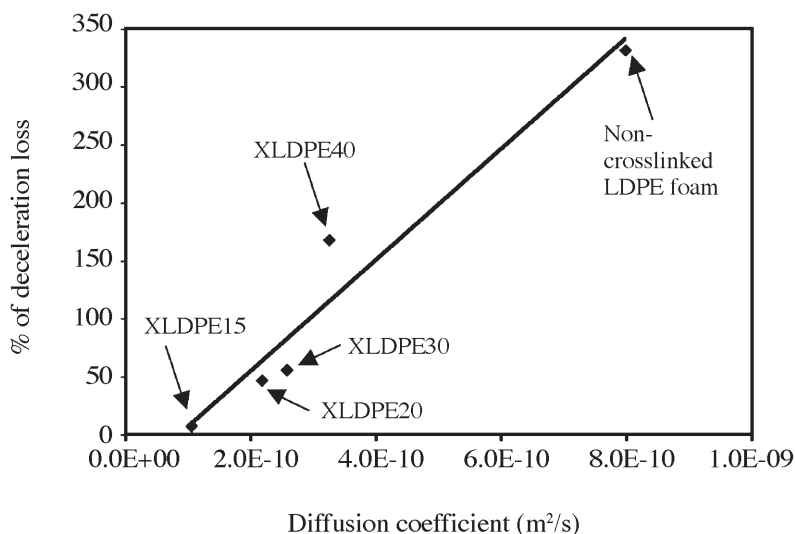


Figure 8. Deceleration loss as a function of the diffusion coefficient. Percentage of deceleration loss = $100 * (\text{deceleration after creep} - \text{deceleration before creep}) / \text{deceleration before creep}$

LDPE foam. The maximum value for the crosslinked LDPE foams (around 170) is reached by the XLDPE40 foam (24 kg/m³).

This behaviour seems not to be a coincidence but reflects a deep aspect of low density closed-cell low density foams impact response, i.e. the great importance of entrapped gas compression in pneumatic cushioning.

8. RECOVERY BEHAVIOUR

If the foam has suffered degassing during the creep test, the recovery shows a peculiar pattern which can be qualitatively observed in Figure 9. In this figure, the images 1 to 4 were registered in the first 24 hours of recovery, meanwhile pictures 5 and 6 were taken one week and a half later and three weeks later respectively.

The foams behaviour can be divided into three main steps:

1. In the first seconds, the recovery is quicker in the middle part of the foam block (picture 1). This effect is related to the adaptation of inner cells to

atmospheric pressure. This step is more evident in high density foams whereas it is nearly imperceptible in low density foams

2. Later, the recovery of this inner part is very slow (pictures 2 to 5), being quicker the recovery of the foam lateral surfaces. This spatial behaviour seems to be related to re-diffusion of the gas inside the foam. At the beginning the middle part recovers quickly because a higher amount of gas was present in this area of the foam, later the gas starts to enter the foam producing recovery in the lateral surfaces. This step presents a high dependency on foam density and crosslinking degree among other structural characteristics, all of them related to gas diffusion.
3. In the last step (picture 6) the cells pressure becomes more homogeneous in the whole sample, which results in a more homogeneous recovery, therefore a smaller curvature in the edges and corners of the sample is showed.

By applying image analysis tracking of the different dots painted on the foam surface (Figure 10a) it is possible to follow the relative displacement of different areas in the foams. With a previous spatial calibration, the distance between dots can be measured. Special conditions are required for this purpose, such as a homogeneous and time-constant illumination and a programmed acquisition of frames with a desired time span. For this purpose, a long-time events chamber was designed and built up using a 1.3 megapixels CMOS camera to acquire programmed frames giving a spatial resolution of 20 pix/mm.

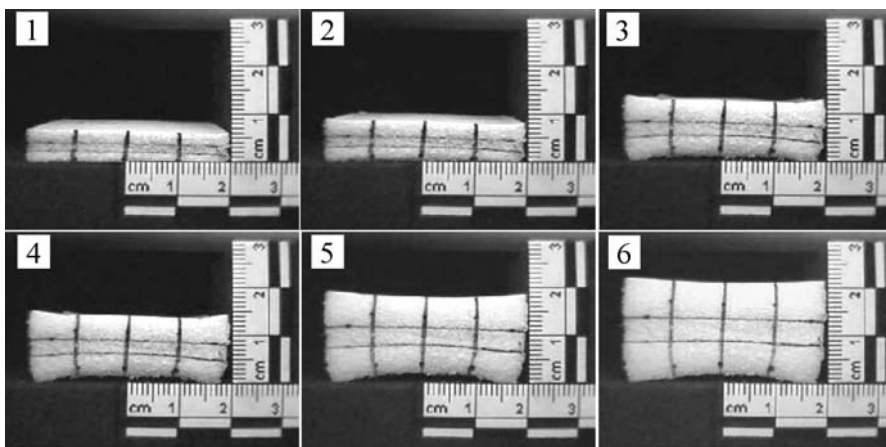


Figure 9. Recovery response of a foam (XLDPE40). Pictures were taken at different times after creep. Picture 1; 0 hours, 2; 0.12 hours, 3; 12 hours 4; 24 hours, 5: 264 hours, 6; 504 hours

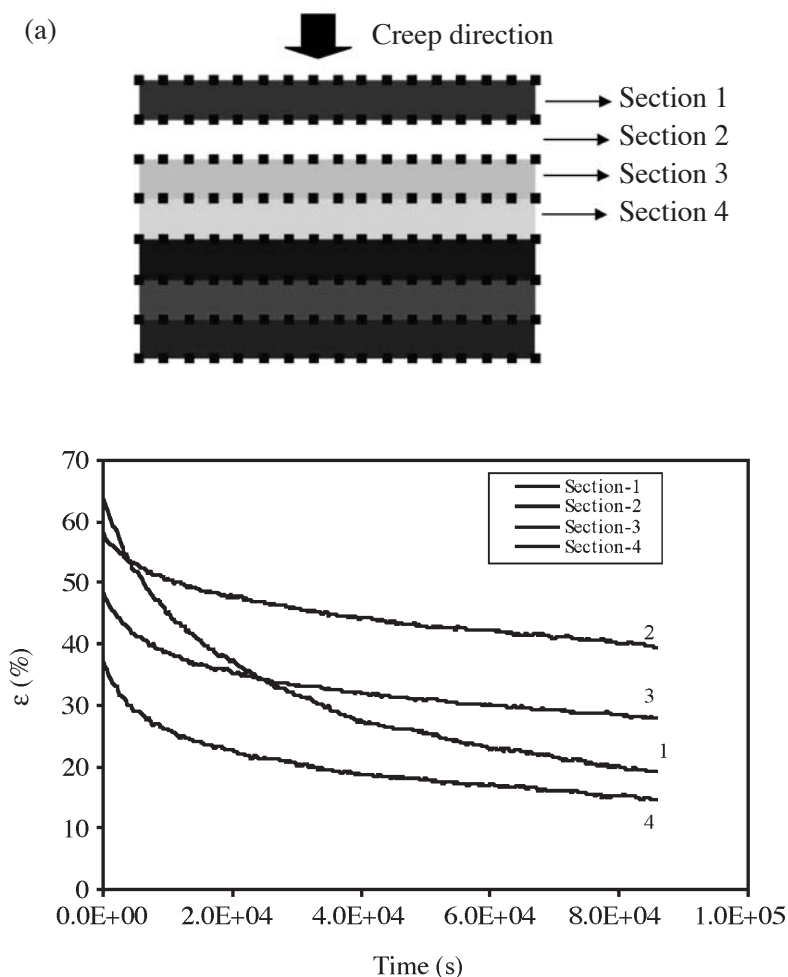


Figure 10. a) Schematic drawing of painted dots on the sample and sections of analysis. b) Recovery curves of sections 1-4 normalized according to the initial distance before creep testing (XLDPE20 foam). The numerical values for each section are obtained as an average of the values for the 12 central points in each section

Dimensional results for the foam XLDPE20 are showed in Figure 10b. The recovery of sections from 1 to 4 are shown, being the strain (ϵ) normalized according to the initial distance, i.e. before the creep compression.

It can be observed a different initial strain of the four sections, which is related to different progressive deformation of different zones during the creep tests.

This fact is probable related to a higher diffusion rate of gas of the most external zones of foam (i.e. creep is also non-homogeneous), because final strain after creep is progressive lower from section 1 to section 4. In addition, and as it was qualitatively mentioned in Figure 9, a higher recovery of section 1 compared to the other sections is clearly observed.

In general terms, it can be assured that the time for recovery is much longer than the time for creep. During creep, there is an applied external pressure, which creates a significant pressure gradient; this is the driving force for gas diffusion. On the other hand, recovery is limited, first because there is no external pressure and second, because the cell walls are partially bended and/or buckled, and some of them could have plastic hinges.

CONCLUSIONS

The proposed method, based on creep experimental data and a theoretical solution of the diffusion equation, allows determining diffusion coefficients in agreement with those previously reported. The dependency of this property with density, chemical composition, crosslinking of the polymeric matrix and sample size has been shown. A reduction in the gas loss is obtained by increasing the density, the crystallinity, increasing the sample size and by using a crosslinked matrix.

It has also been proved that gas diffusion is a relatively fast process for these low density foams, in which the majority of gas escapes in a time scale of seven days. This fact has important effects such as:

1. There is an important loss of performance under impact tests, which is closely related to the diffusion coefficient.
2. Recovery after creep is a non-homogeneous process which for low density foams and high static stresses and creep times (i.e. if gas diffusion takes place during creep) seems to be controlled by re-diffusion of the gas into the foam.

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