Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 3105–3110

polymer

www.elsevier.com/locate/polymer

Effective diffusion coefficient for the gas contained in closed cell polyethylene-based foams subjected to compressive creep tests

J.L. Ruiz-Herrero, M.A. Rodríguez-Pérez*, J.A. de Saja

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain

Received 10 December 2004; received in revised form 19 January 2005; accepted 19 January 2005
Available online 3 March 2005

Abstract

In this paper, a new method to obtain the effective diffusion coefficient of the gas contained in closed cell foams under static loading is presented. Compressive creep experiments were performed on six low-density polyethylene (LDPE) and two polyethylene-*co*-vinyl acetate (EVA) foams of different densities using a home-designed compressive creep apparatus. The modelling of the evolution of pressure inside the cells was performed using an isothermal compression model. The effective diffusion coefficients were obtained from pressure decrease with time using an analytical solution of the diffusion equation. The values obtained agreed with those in literature and were dependent on both foam density and chemical composition.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Polyethylene foams; Diffusion coefficient; Creep testing

1. Introduction

Closed cell polymeric foams consist of gas bubbles separated by a thin membrane of a continuous solid phase that can be rigid or flexible (Fig. 1) [1,2]. Such versatile materials have a wide range of applications, where its unique combination of properties is exploited [3]. In some of these applications, like structural, cushioning and packaging, the foams are subjected to long-term static loading that could affect its mechanical properties due to, on the one hand, the plastic deformation of the matrix and on the other hand, the gas diffusion from the cells [4]. In addition, it is well established that gas diffusion, often called ageing, affects the thermal insulation capability of foams [5,6]. Therefore, understanding and modelling the creep response, and the closely related degassing behaviour under static loads, is of major importance from both fundamental and practical viewpoints [2].

Flexible foam creep response is dominated by the polymer viscoelasticity if the stress is less than the yield stress, but over that point, gas compression takes an increasingly higher proportion of the load and outward diffusion of the gas contained in the cells takes place [3,7].

There have been some attempts to relate the creep behaviour of cellular solids to their cellular structure and base material properties. For example, several authors have proposed [1,8,9] modelling the foam creep response in terms of the creep behaviour of the matrix, predicting a creep-rate proportional to $(\rho_f/\rho_s)^{-n}$ where n is an empirical constant that accounts for the creep behaviour of the polymeric matrix and ρ_f/ρ_s is the relative density.

But in flexible closed-cell polymeric foams, loaded in the post-collapse region, there is also a contribution of gas escape to the creep response, which depends on the foam density and polymer diffusivity to the gas [7,10].

Pilon et al. reviewed the diffusion models in closed-cell polymeric foams [2] and Briscoe studied experimentally and theoretically the degassing behaviour of LDPE high density foams during storage [11], obtaining effective diffusion coefficients varying between 10^{-10} and 10^{-11} m^2/s depending on the matrix volume fraction (relative density).

Mills [4,7] using a discrete model predicted a diffusion coefficient for the undeformed foam given by:

$$D_{\mathrm{eff}} = \frac{6Pp_a}{f_f R} \tag{1}$$

---

* Corresponding author. Tel.: +34 983 1840 35; fax: +34 983 423 192.
E-mail address: marrod@fmc.uva.es (M.A. Rodríguez-Pérez).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.01.093

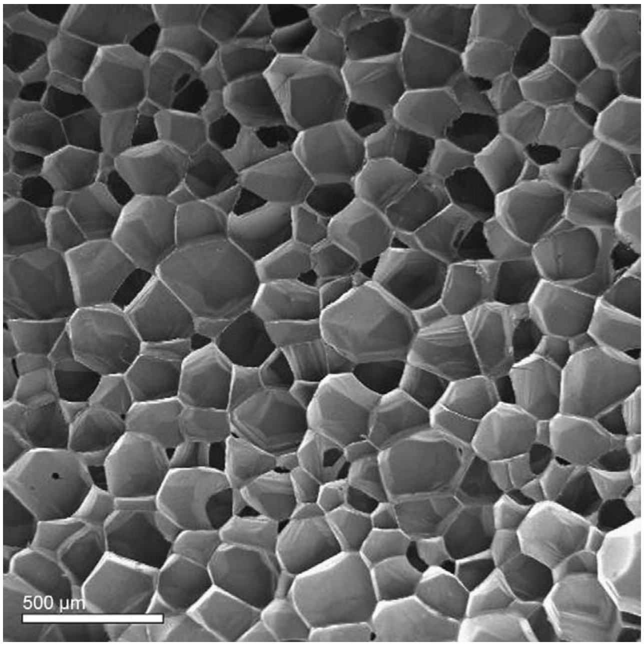

Fig. 1. Cellular structure of one of the foams (Pe40).

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.

The values for the effective diffusion coefficients of gas contained in the cells for LDPE (densities 66 and 22 Kg/m^3) and EVA (density 34 kg/m^3) foams have been predicted theoretically by Mills and Gillchrist [7] and were reported to be: D_{eff} (LDPE, $\rho_f = 66$ Kg/m^3) $\sim 250 \times 10^{-12}$ m^2/s, D_{eff} (LDPE, $\rho_f = 22$ Kg/m^3) $\sim 500 \times 10^{-12}$ m^2/s and D_{eff} (EVA, $\rho_f = 34$ Kg/m^3) $\sim 1000 \times 10^{-12}$ m^2/s.

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. As far as we know, a systematic experimental study has not been published previously.

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.

2. Method

2.1. Materials

The main foam characteristics are summarized in Table 1. Seven of the studied foams were produced by a two stage press moulding procedure [12,13], using azodicarbonamide and dicumyl peroxide as foaming and cross-linking agents. The foam called 'copex' was produced by means of an extrusion process and do not present a cross-linked base polymer. The EVA foams presented 19% vinyl acetate content. Finally, the foam called 'Pe20N' presented a $5 \pm 0.5\%$ carbon black content as determined by thermogravimetric (TGA) measurements.

2.2. Differential scanning calorimetry (DSC)

Thermal properties were studied by using a Mettler DSC30 differential scanning calorimeter. The weights of foam samples were approximately 3.5 mg. The experiments were carried out between −40 and 200 °C at a heating rate of 10 °C/min. Two characteristic properties of the base polymer were obtained: the melting point (T_m) and the crystallinity. The melting point was taken as the minimum of the melt peak in the enthalpy curve and the crystallinity was calculated from the DSC curves by dividing the measured heat of fusion by that of 100% crystalline polyethylene (288 J/g) [14].

2.3. Scanning electron microscopy (SEM)

Quantitative image analysis was used to obtain the mean cell size and face (cell wall) thickness. For this purpose, foam samples were microtomed at low temperature to provide a smooth surface, which after gold coating, was examined by SEM using a JEOL JSM 820. Apparent mean cell size was measured by calculating the number of cells that intersected each reference line, and dividing the appropriate reference length by the number of cells [15]. The results obtained were multiplied by 1.62 to take into account the relationship between the average measured length of the randomly truncated cells and the real diameter of the cell [16]. The procedure was repeated in the three

Table 1
Characteristics for the foams under study foam: 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 (μm)	δ (μm)	X_c(%)	T_m(°C)
Pe15 cross-linked LDPE	59.51 ± 3.19		2.0 ± 0.1	34.4 ± 0.2	108.9 ± 0.39
Pe20 cross-linked LDPE	36.91 ± 2.11	213.5 ± 8.8	1.5 ± 0.1	35.2 ± 1.36	108.9 ± 0.44
Pe30 cross-linked LDPE	25.46 ± 1.06	255.2 ± 8.2	1.2 ± 0.1	36.7 ± 0.79	108.8 ± 0.33
Pe40 cross-linked LDPE	23.80 ± 1.40	263.4 ± 23.9	1.1 ± 0.1	30.7 ± 1.01	108.8 ± 0.21
Co20 cross-linked EVA	43.51 ± 1.35	214.3 ± 15.4	1.4 ± 0.1	22.7 ± 1.71	86.6 ± 0.75
Co30 cross-linked EVA	28.73 ± 1.01	246.6 ± 13.1	1.1 ± 0.1	22.8 ± 1.10	88.2 ± 0.78
Pe20N cross-linked LDPE	40.45 ± 1.53	212.1 ± 9.0	1.55 ± 0.1	39.1 ± 0.96	109.7 ± 0.32
Copex LDPE	35.59 ± 1.40	~ 2000	–	31.5 ± 1.15	108.4 ± 0.56

main directions of the foams (x, y and z). The mean cell size was calculated as the average of the cell size in the three directions. The thickness of 20 cell walls, randomly chosen, was measured. Cell wall thickness was estimated as the average of these values.

2.4. Creep experiments

A home-designed compressive creep apparatus was used to measure the response of the foams to an applied constant stress over a 7 days period. Two creep rigs are shown in Fig. 2. In each of them, the thickness of the foam is monitored with a linear variable displacement transducer (LVDT) which is connected to a computer.

The sample size was $40\times40\times30\ \mathrm{mm}^3$ except for the copex and Pe20N foams. For these materials slightly bigger samples $50\times50\times50\ \mathrm{mm}^3$ were used. For each foam, experiments at five different stresses were carried out. Temperature was 23 ± 2 °C.

3. Results

3.1. Characterization

The materials under study were almost isotropic (i.e. cell size was very similar in different directions, Fig. 1). The mean cell size for foams is largely dependent upon the manufacturing process [12]. As it can be seen in Table 1, for the LDPE cross-linked foams studied, 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 level [12,13].

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 cross-linked 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 cross-linked LDPE foams indicate similar grades of the LDPE used in the manufacturing process of all these foams.

3.2. Creep

The observed response in the creep tests is an instantaneous strain, that depends upon foam density and load applied, followed by a minor strain increase as a function of creep time (Fig. 3).

For closed-cell foams loaded in the post-collapse region (plateau), assuming the isothermal compression of the gas and non-lateral expansion, the uniaxial compressive stress (σ) can be obtained from the expression [17,3,1]:

$$\sigma = \sigma_0 + \frac{P_o\varepsilon}{1-\varepsilon-\rho_f/\rho_s} \qquad (2)$$

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

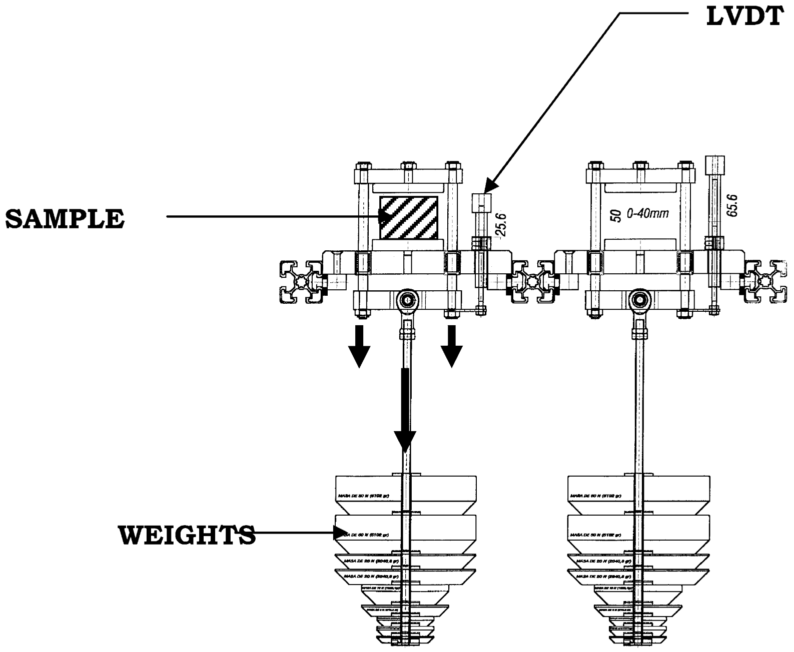

Fig. 2. Two compressive creep rigs.

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) curves were obtained, for all the foams, plotting the compressive stress 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.

As it can be observed in Fig. 4, the pressure inside the cells decreased with creep time.

To obtain the values of the initial pressure inside the undeformed foam the values of pressure were fitted to an exponential decreasing function (Fig. 5). The values of the initial pressures for the LDPE foams are collected in Table 2.

During the 7 days experiment, the pressure was reduced by a factor that depends on density; for example, for the lowest density foam Pe40 an 88% reduction of pressure is obtained ($P/P_0=0.12$). The reduction in the gas content in the cells can be obtained from pressure decrease through the equation:

$$\frac{n}{n_0}=\frac{P}{P_0}\,\frac{(1-\varepsilon_{\max})\rho_s-\rho_f}{\rho_s-\rho_f}\,\frac{1}{1-\varepsilon_{\max}} \tag{3}$$

where n and n_0 are the gas content inside the cells after and before the creep experiment, ε_m is the maximum deformation, 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.

Therefore in 7 days experiment almost all the gas (90% for the Pe40 foam at a static stress of 73.3 kPa) has escaped from the foam.

The effective diffusion coefficients can be obtained from the evolution of pressure with time using a solution of the diffusion equation proposed by Svanström et al. [18] and valid for foam slabs.

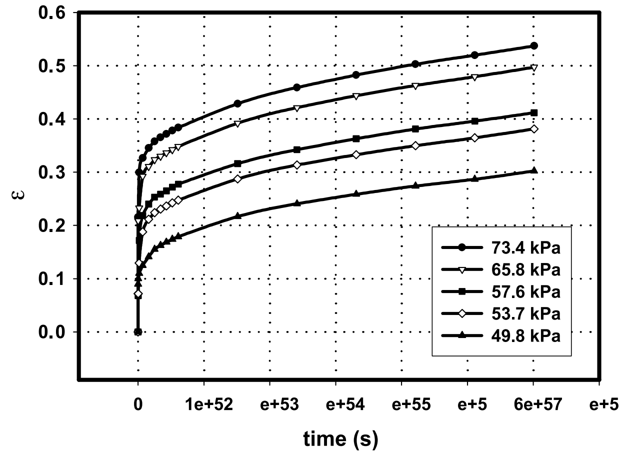

Fig. 3. Creep response of Pe20N foam at five different applied stresses.

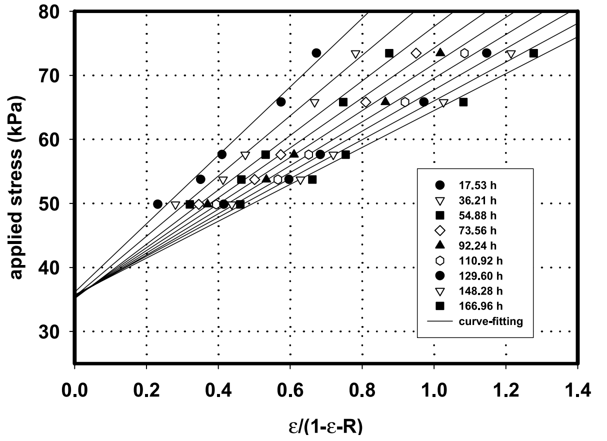

Fig. 4. Typical isochronous (applied stress) vs (gas volumetric strain) curves for a Pe20N foam.

$$D_{\text{eff}}=-\frac{L^2}{\pi^2}\,\frac{d\{\ln[(P_{\text{total}}\pi^2)/(8P^0)]\}}{\mathrm{d}t} \tag{4}$$

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.

Typical curves for $\ln(P^2\pi/P^0)$ are shown in Fig. 6. These curves fitted well to linear ones. Their slopes are closely related to effective diffusion coefficients (Table 3). In Fig. 7 the values obtained for D_{eff} are plotted as a function of foam density.

4. Discussion

The values for the effective diffusion coefficients were approximately of the same order of magnitude than those found in literature and, although there is some scatter, (Fig. 8) the values for the LDPE foams with the same sample size, varied inversely with foam density in agreement with the predictions of the calculations of Mills (Eq. (1)).

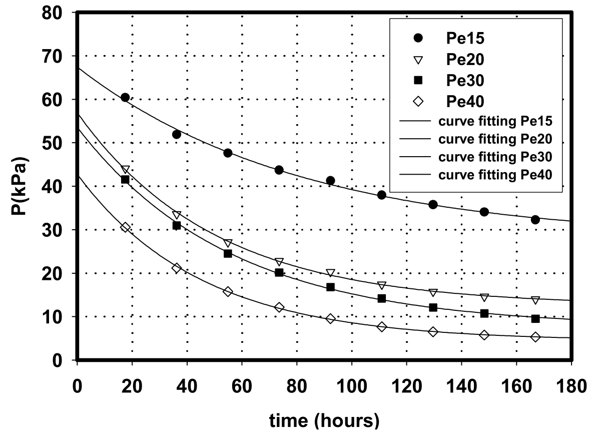

Fig. 5. Fitting of the pressure vs time curve to the function $P=P^0+a\mathrm{e}^{-bt}$.

Table 2
Initial gas pressure for the foams before the creep experiments

Foam	Pe15	Pe20	Pe30	Pe40	Pe20N	Co20	Co30	Copex
P_0 (kPa)	70.9±3.3	59.1±1.9	55.8±1.6	44.0±1.5	61.4±1.1	60.4±0.5	69.1±0.5	50.5±2.0

Table 3
Effective diffusion coefficients for the studied foams

Foam	Pe15	Pe20	Pe30	Pe40	Pe20N	Copex	Co20	Co30
D_{eff} ($\mathrm{m^2/s}$)	1.04×10^{-10}	2.18×10^{-10}	2.55×10^{-10}	3.24×10^{-10}	2.61×10^{-10}	7.96×10^{-10}	5.14×10^{-10}	8.66×10^{-10}

The EVA foams presented values for D_{eff} higher than the LDPE ones in accordance with 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 [19]. Therefore, gas escape occurs at shorter times for equal sized blocks at the same stress. The non-crosslinked copex foam presented values for effective diffusion coefficient higher than the cross-linked LDPE based ones. This difference probably arises from the different segment mobility in the amorphous phase of the base polymer due to crosslinking.

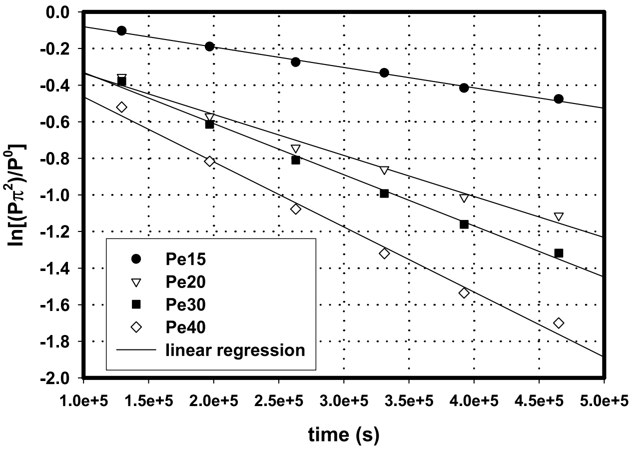

Fig. 6. Curves for the logarithmic relative pressure decrease as a function of time for the equal sized LDPE foams.

It was noticed that the pressure inside the cells before the experiment was lower than atmospheric. Clutton [3] states that this fact may arise from the reduction in pressure during the cooling stage of manufacture, and the long times for pressure to equilibrate. Another reason for this result could be the effect of the Poisson's ratio on the compressive creep response of foams. Eq. (2) was deduced assuming zero lateral expansion. If the analysis is repeated assuming that Poisson ratio is non-negligible, the slope of the stress vs volumetric strain is $P_0(1-2\nu)$, therefore values of the slope different from atmospheric pressure could be related to a non-zero value of ν. However, the previous discussion on the absolute value of P_0 does not affect the definition of D_{eff} proposed by Svanström et al. which uses the relative pressure decrease (P/P_0).

When creep continues to high strains, the pressure decrease (in logarithmic scale) was no longer linear. This may arise from the fact that when creep continues, the majority of the gas in the cells has escaped [7].

5. Conclusions

The proposed method, based on creep experimental data

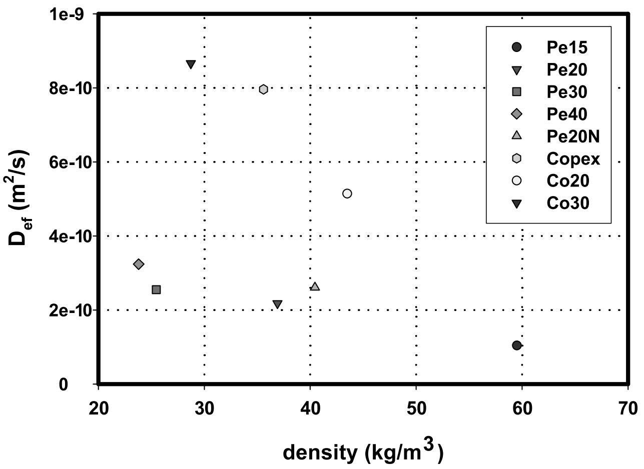

Fig. 7. Effective diffusion coefficients values for the foams under study.

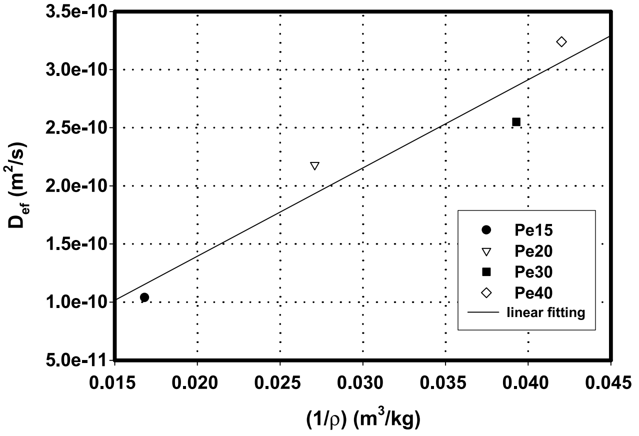

Fig. 8. Effective diffusion coefficients for the equal sized LDPE foams as a function of ($1/\rho$).

and a theoretical solution of the diffusion equation, predicts diffusion coefficients in agreement with those previously reported. The dependency of this property with density, chemical composition and crosslinking of the polymeric matrix has been shown. A reduction in the gas loss is obtained by increasing the density, the crystallinity and by using a cross-linked matrix.

The gas diffusion is a relatively quick process for these low density foams, in which the majority of gas escapes in a time scale of 7 days.

Acknowledgements

Thanks are due to MICROCEL S.A. for kindly providing the samples under study and to the Local Government (Junta de Castilla y León) and Spanish Ministry of Education and Science for financial support (VA026 /03 and MAT 2003-06797).

References

[1] Gibson LJ, Ashby MF. Cellular solids: structure and properties. Oxford, England: Pergamon Press; 1997.
[2] Pilon L, Fedorov AG, Viskanta R. J Cell Plast 2000;36:451–74.
[3] Clutton EQ, Rice GN. Cellular polymers conference, Rapra Technology 1991;99–107.
[4] Mills NJ, Rodríguez-Pérez MA. Cell Polym 2001;20(2):79–100.
[5] Hoogendorn. Thermal ageing. In: Hilyard NC, Cunninham A, editors. Low density cellular plastics; physical basis of behaviour. New York: Chapman & Hall; 1994.
[6] Bart GCJ, Du Cauzé de Nazelle GMR. J Cell Plast 1993;29:29–42.
[7] Mills NJ, Gilchrist A. J Cell Plast 1997;33(3):264–92.
[8] Andrews EW, Gibson LJ, Ashby MF. Acta Materialia 1999;10:2853–63.
[9] Cocks ACF, Ashby MF. Acta Materialia 2000;48:3395–400.
[10] Verdejo R. Thesis, School of Engineering Metallurgy and Materials. University of Birmingham 2003.
[11] Briscoe BJ, Savvas T. Adv Polym Technol 1998;17(2):87–106.
[12] Park CP. Polyolefin foam. In: Klempner D, Frisch KC, editors. Handbook of polymeric foams and foam technology. Munich: Carl Hanser Verlag; 1991.
[13] Puri RR, Collington KT. Cell Polym 1988;7:219–31.
[14] Wunderlich B. Macromolecular physics. vol. 2. New York: Academic Press; 1976.
[15] Sims GLA, Khunniteekool C. Cell Polym 1994;13:137–46.
[16] ASTM D3576, Annual Book of ASTM Standards. vol. 8.02, 1994.
[17] Rusch KC. J Appl Polym Sci 1969;13:2297–311.
[18] Svanström M, Ramnäs O, Olsson M, Jarfelt U. J Cell Polym 1997;16(3):182–93.
[19] Mills NJ. Rapra Review Reports 2003;14(11).