Conference Proceedings
A FLEXIBLE BARRIER TO AVOID SOLID SKIN APPEARANCE IN CELLULAR POLYMERS PRODUCED BY GAS DISSOLUTION FOAMING

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Abstract

Gas dissolution foaming is one of the most employed methods to produce polymer foams. Despite all the advantages of this environmentally friendly method based on physical gas dissolution, the obtained cellular polymers generally present a non-foamed solid skin surrounding the foamed core. This feature is related to the diffusivity mechanisms which are involved in the pressure drop stage and represents a significant drawback, limiting many potential applications of these materials. This work proposes the incorporation of a flexible gas diffusion barrier during the foaming process which allows reducing the solid skin without limiting the expansion during the foaming stage.

Introduction

Polymer foams and their fabrication methods have been widely studied in the last decades due to the interesting properties presented by these materials. Particularly, gas dissolution foaming has become one of the most employed methods to produce from micro to nanocellular foams, obtaining low-density foams with homogenous cellular structures from several polymer [1–5].

Gas dissolution foaming is considered a green procedure based on the physical dissolution of the gas into the polymer. In contrast with other fabrication methods, gas dissolution foaming uses a harmless production route without using dangerous pollutants such as organic solvents or generating hazardous residues [6].

In despite of the benefits and the versatility of the gas dissolution foaming compared to other methods, foams produced by this technique show a characteristic drawback. A non-foamed skin with a thickness of tens to hundreds of microns is generally formed in the borders of the bulk samples during the foaming process. In addition, in the particular case of thinner samples, e.g., films with thicknesses around or below hundreds of microns, foaming is difficult and the expansion ratios very limited as a results of a solid skin thickness with comparable dimensions to the thickness of the sample (i.e., there is no, or just scarce foamed regions inside the sample) [7]. Moreover, the presence of the outer solid skins supposes a clear limitation for the use of these materials in several applications. For instance, the interconnection of the cellular structure with the external medium would allow employing them as filters, as well as in catalysis, in gas storage, or as sensors [8–12].

In the previous literature, the challenge of reducing and eliminating the outer solid skins has been studied by several authors with the aim of interconnecting the inner cellular structure with the external medium. Most of them use \textit{a posteriori} techniques to eliminate the solid skin by drilling, milling or polishing [13–16]. On the other hand, a few works have tried to avoid the appearance of the outer solid skin during the foaming process. According to the previous knowledge, outer solid skins are produced by the fast diffusion of the gas from the external layers of the polymer samples to the outside during the desorption stage prior to foaming. As a result of this diffusion there are low gas concentration levels in the borders of the sample. Thus, the formation of the cellular structure is hindered in those regions. Therefore, some authors tried to limit the gas diffusivity in order to avoid the appearance of the outer solid skins. Siripurapu et al. [17] used a rigid metallic mould which restricts the gas diffusion through the faces with largest areas in order to foam thin films. However, foaming occurs inside a rigid mould that limits the expansion of the film. Ge et al. [18] used polyamide layers covering a thermoplastic polyurethane ultrathin film to generate pores with similar magnitude of the film thickness (20 µm). These polyamide layers act as heterogenous nucleating agents by surface contact, not as gas diffusion barrier. So, this technique is not available for thicker samples. In addition, other approach involving a gas diffusion barrier has allowed producing hollow micrometric and nanometric polymeric systems with porous surfaces by coating them with poly-vinyl alcohol [19,20].
However, those approaches have been just proved either in ultrathin films or in micrometric systems but not in bulk samples, aiming to reduce the outer solid skins or even increase their expansion. Therefore, this work is focused on developing a general approach to reduce the thickness of the outer solid skins which appear in polymer foams fabricated by gas dissolution foaming. Our approach is based on introducing a gas diffusion barrier over the polymer surfaces in order to reduce the gas diffusion through these faces. Thus, the gas concentration in the borders is maximized to achieve the foaming in these regions. Besides, this technique can be employed either in bulk samples or in thin films, without compromising the polymer expansion by using a flexible gas diffusion barrier.

**Experimental methods**

**Materials**

Poly-methyl methacrylate (PMMA) ALTUGLAS V82ST was kindly supplied by ARKEMA (Colombes, France). Poly-vinyl alcohol (PVOH) MOWIFLEX C17 was purchased from Kuraray Europe (Hattersheim am Main, Deutschland). A medical grade of CO₂ (99.9% purity) was employed as a blowing agent for foaming experiments.

**PVOH incorporation**

PMMA was received in the form of pellets, which were thermoformed with a hot plate press in sheets of 0.5 mm. On the other hand, PVOH films were prepared by a solvent casting method with 200 microns of thickness. The PVOH films were incorporated by compressing them over the PMMA surfaces, applying pressure and temperature with a hot plate press. The resulting samples show a sandwich-like structure with just one surface or both covered by PVOH.

**Gas dissolution foaming**

Samples were foamed in a high-pressure vessel (model PARR 4760) provided by Parr Instrument Company (Moline, IL, USA) according to the gas dissolution foaming procedures (i.e., saturation, desorption, and foaming stages). Saturation pressure and temperature was fixed respectively at 30 MPa and 25 °C for all experiments. The saturation time was fixed between 24 to 72 hour to ensure the gas saturation of the PMMA. Then, the foaming stage was carried out in an oil bath at 60 °C during 1 minute in order to prevent the solution of the PVOH in water.

**Characterization techniques**

Density of solid samples was measured with a gas pycnometer (Mod. AccuPyc II 1340, Micromeritics, Norcross, GA, USA), and the density of the foams was measured using the water-displacement method based on Archimedes’ principle. Relative density was calculated as the relation between foam density and solid density.

The structure of the foamed samples was observed by Scanning Electron Microscopy (SEM) (HITACHI FlexSEM 1000). First, samples were cooled in liquid nitrogen and then fractured. Surfaces to visualize (cross-section and external surfaces with or without PVOH) were coated with gold using a sputter coater (model SDC 005, Balzers Union, Balzers, Liechtenstein). Measurements of non-foamed skin were directly performed from SEM micrographs of the cross-section employing ImageJ/FIJI [21]. Several measures from the external edge of the sample to the homogenous cellular structure were carried out, neglecting lonely precedent pores. From these measurements it was obtained the thickness ratio of the solid regions regarding the total thickness of the sample (SS).

Also, the relative density of the homogeneous foamed core of PMMA samples was estimated. The estimated relative density (ERD) was calculated taking into account the overall relative density (RD) of the sample, the ratio of the solid skins (SS), and the relative density of the solid skins (ρs, ≈ 1) (Equation 1).

$$ERD = \frac{RD - SS \times \rho_S}{1 - SS}$$

**Results**

The effect of the PVOH as a gas diffusion barrier was studied by coating one of the external surfaces of a PMMA sample, leaving the other one without PVOH coating (Figure 1).

The cross-section SEM micrograph of Figure 1 shows the cellular structure of the PMMA sample, which presents a quite a heterogeneous cellular structure. On the one hand, the top-half of the sample clearly presents a non-foamed skin which represents almost 25% of the sample with a solid thickness of around 50 μm. On the other hand, the bottom-half is almost completely foamed. Therefore, the PVOH barrier has kept an appropriate amount of gas, i.e., enough to induce the foaming on the bottom half of the sample. On the contrary, the gas located in the top half leaks through the top surface without PVOH. It must be noted that no significant solid skin appears on the bottom of the sample, highlighting the great effectiveness of PVOH as a gas diffusion barrier.

Besides, cellular structure shows a cell size and density gradient along the sample thickness, which is also promoted by the diffusion phenomenon. The number of cells per unit volume and their expansion are closely linked to the gas concentration into the polymer [6]. Thus, the gradient in gas concentration, induced by the gas diffusion out of the sample through the surfaces without PVOH,
leaves a broad cell size and cell density distributions along the thickness of the sample.

Figure 1. SEM micrograph of the cross-section of a PMMA sample foamed by using the PVOH approach. The gas barrier was only incorporated over the outer bottom surface.

The gradient in the cellular structure can be related to the gas concentration, being the regions with larger cell densities and porosities those with higher remaining gas concentration at the foaming stage. Then, the gradient of cell size and cell density shown in Figure 1 allows a qualitative estimation of the remaining gas concentration profile in the sample at the foaming stage. This profile is illustrated in Figure 2, together with the initial gas concentration (green dashed line) and the gas concentration threshold required to achieve a cellular structure (red dashed line). This gas concentration profile as a function of the sample thickness was plotted according to the cellular structure showed in Figure 1.

The proposed concentration profile is quite diverse regarding the concentration profiles usually achieved using the gas dissolution foaming technique. Typically, the highest gas concentration at the foaming stage is reached in the centre of the polymer sample, as the gas in the outer layers quickly diffuses out of the sample. However, in this example the presence of the gas diffusion barrier just in one surface allows remaining an appropriate gas concentration in the bottom-half while most of the gas in the centre and in the top-half diffuses through the top surface. Therefore, the gas concentration at the foaming time is lower in the centre than in the region close to the gas diffusion barrier. According to that concentration profile (Figure 2), regions with a gas concentration level below the threshold limit to reach foaming (i.e., red dashed line) do not show any cellular structure, corresponding to the thick top solid skin shown in Figure 1.

Once the effectiveness of the gas diffusion barrier was evidenced by this comparative test, this approach was further studied by applying the PVOH in both top and bottom external surfaces and comparing the foaming behavior at the same conditions of PMMA samples with and without the PVOH coating.

First, PMMA bulk samples foamed by traditional gas dissolution foaming show a core with a quite homogeneous cellular structure surrounded by non-foamed solid skins with thicknesses around 80 microns (Figure 3). On the other hand, PMMA samples with PVOH coating (Figure 4) show a homogenous cellular structure from the centre to the edges, proving the exceptional effectiveness of the gas diffusion barrier applied on both outer surfaces, top and bottom.
In these cases, the estimated gas concentration profiles present quite differences that can be analyzed by the following illustrations (Figure 5 and Figure 6). First, the gas concentration in the borders of the PMMA sample without PVOH has decreased below the threshold limit to foam due to the fast diffusion of the gas in these regions. Therefore, non-foamed skins were formed in the surroundings of the polymer. The core shows an almost constant gas concentration which results in homogenous cellular structure until the sharp decrease in the concentration profile. This reduction induces the formation of large bubbles prior to the non-foamed solid skins.

On the other hand, the gas diffusion barrier has allowed maintaining the gas concentration over that threshold in the whole sample (Figure 6), obtaining a homogenous cellular structure until the borders. Only a region very close to the border presents less cell nucleation density than the homogeneous core, related to the sharp reduction in the concentration profile shown in the edges (Figure 6). In any case, the significant gas loss in the outer layers, typical of this technique, have been avoided by the employment of the gas diffusion barrier, obtaining a very thin densified skin.

The reduction and elimination of the outer solid skins suppose several advantages for these materials. The most evident is that the reduction of the non-foamed solid skin implies an enhancement of the foamed volume of the samples, and thus, a decrease in their relative density.

Table 1 shows the comparison between the relative density, the volume percentage of solid skins, and the
estimated relative density reached by the core of the samples shown in Figure 3 and Figure 4.

Table 1. Comparison of the relative density, the percentage of the non-foamed solid skins, and the estimated relative density of the core for foamed samples obtained with and without using the gas diffusion barrier.

<table>
<thead>
<tr>
<th></th>
<th>Relative density</th>
<th>% of solid skin</th>
<th>Estimated relative density (ERD)</th>
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<tbody>
<tr>
<td>PMMA</td>
<td>0.504</td>
<td>21.2</td>
<td>0.370</td>
</tr>
<tr>
<td>PMMA with PVOH coating</td>
<td>0.353</td>
<td>2.6</td>
<td>0.336</td>
</tr>
</tbody>
</table>

As expected, the overall relative density is reduced by incorporating the gas diffusion barrier on the outer surfaces of PMMA (i.e., decreasing the non-foamed solid skins from 21.2 to 2.6 %). It can be noted that the estimated relative density of the core of the PMMA samples coated with PVOH is similar to their measured overall relative density, evidencing the negligible presence of solid skins. Most importantly, the achieved density is lower than that of the foamed core of the PMMA samples without PVOH coating. Therefore, the PVOH coating not only allows decreasing the overall relative density by reducing the solid skins thickness, but also promotes a higher expansion of the core.

Besides, the reduction and elimination of the non-foamed solid skins could offer the possibility of interconnecting the inner cellular structure with the external medium. This feature would extend the range of applications of these cellular polymers. For instance, employing them in some potential applications which requires that interconnection such as in filtration, in gas storage, in catalysis, or as sensors. This potential feature was also studied following the proposed approach. With this aim, the external surfaces of the coated and non-coated PMMA bulk foamed samples were studied by SEM (Figure 8 and Figure 9).

The surface of the foamed PMMA without PVOH (Figure 7) shows the typical smooth appearance of the solid polymer which correspond with the non-foamed solid skins. In contrast, the incorporation of the gas diffusion barrier provides high porosity on the surface of the PMMA samples coated with PVOH. In addition to the remaining higher gas concentration in the edges of these samples, the porous structure on the surface could be promoted by the interface of both polymers acting as a preferable location site of the CO$_2$ molecules, i.e., as heterogeneous nucleating sites [18]. In this way, the accumulation of gas molecules in the interface could be beneficial to achieve cells not only in the borders but also on the surface, interconnecting the inner cellular structure with the external medium.

Figure 8. SEM micrograph of the outer surface of PMMA bulk samples foamed without using the PVOH coating.

Figure 9. SEM micrograph of the outer surface of PMMA bulk samples foamed using the PVOH coating.

Therefore, the use of PVOH as gas diffusion barrier prove to be a successful approach to overcome the limitations related to the appearance of the outer solid skins by gas dissolution foaming. Also, large expansions were reached by using a flexible diffusion barrier instead of the stiff barriers employed in the past [22], which clearly hindered obtaining low-density cellular polymers. Moreover, the obtained results have confirmed the possibility of inducing the formation of cells directly on the external surfaces, which could interconnect the inner cellular structure with the external medium. Future work, aiming to reach these feature with high-porosity nanocellular polymers [23,24] could result in materials with excellent capability to act in promising applications such as membranes, filters or sensors.

Conclusions

A novel approach was successfully introduced in the classical gas dissolution foaming technique in order to
avoid the appearance of the non-foamed solid skins. Flexible gas diffusion barriers located on the principal surfaces of the polymer samples were used to reduce the gas diffusivity during the desorption step, keeping gas concentrations high enough in the edges to foam these regions.

In this way, non-foamed solid skins were significantly decreased obtaining PMMA samples almost fully foamed, and also significantly reducing the overall relative density. Besides, the gas diffusion barrier induced a heterogeneous nucleation in the polymer surfaces by the contact between both polymers creating a large quantity of pores. Therefore, this feature could allow interconnecting the inner cellular structure with the external medium, extending the range of applications of cellular polymers produced by gas dissolution foaming, which are currently limited for applications such as filtration, gas storage, catalysis, or as sensors.

Acknowledgements:
Financial support from Spanish Ministry of Science and Innovation FPI grant PRE2019-088820 (D. Cuadra-Rodriguez). Financial assistance from the Junta de Castille and Leon (VA202P20), Spanish Ministry of Science, Innovation and Universities (RTI2018-098749-B-I00) and from EREN (Ente Regional de la Energia de Castilla y Leon EREN_2019_L4_UVA) is gratefully acknowledged.

References
21. Abràmoff, M.D.; Magalhães, P.J.; Ram, S.J.
