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Production of non-crosslinked thermoplastic foams with a controlled density and a wide range of cellular structures

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ABSTRACT: A novel foaming route, with respect to existing industrial foaming processes, called "Improved Compression Molding" (ICM), which allows producing non-crosslinked thermoplastic foams in a wide density range, is described in this work. This process is different from others because it is possible to control independently density and cellular structure and therefore, tailored cellular polymers can be produced. To understand the process, a collection of polypropylene foams, with relative densities ranging from 0.3 to 0.6 were produced. The influence of foaming parameters, on foams microstructure and mechanical response was analyzed. Results revealed that for similar densities, foams with different open cell content and cell size can be achieved. In addition, it was proved that mechanical behavior strongly depends on the degree of interconnectivity of the cells. The analysis of the relative mechanical properties allowed determining the influence of microstructure on mechanical behavior as well as quantifying the efficiency of the foaming process to produce light-weight stiff materials. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42324.

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INTRODUCTION

Polymeric foams can be defined as two-phase materials in which a gas is dispersed in a continuous macromolecular phase.[1] Due to their outstanding properties, thermoplastic foams have become essential items and although they are mainly used as thermal insulators or impact absorbing elements, they have found applications in almost every field.[2–4]

Since their development in 1940s, both scientific and industrial communities have focused their attention on the development of foaming technologies able to satisfy the growing demand of thermoplastic foamed products.[3] Nowadays, no single foaming method dominates thermoplastic foam manufacture, and both continuous and batch processes are operated using either chemical or physical blowing agents. The most commonly used foaming processes to produce thermoplastic foams are extrusion, injection molding, compression molding or gas dissolution foaming in a batch process.[1–5]

The selection of the foaming process is conditioned mainly by the final application of the material which at the same time strongly depends on its relative density (i.e. the density of the foam divided by that of the corresponding solid). It is well known that the foaming process itself as well as the intrinsic characteristics of the polymeric matrix heavily determines the cellular structure of the foamed product.[4,5]

According to this, depending on the final application of the foam and the desired expansion ratio, the most suitable process is chosen. Thus, extrusion using a physical blowing agent is a good choice to produce low or ultra-low density foamed sheets or profiles for heat insulation or packaging applications.[3] Injection molding is the best election to produce net-shaped foamed parts. However, density reductions are limited to a 40%, and in addition this weight reduction strongly depends on size and shape of the part.[6] The gas dissolution foaming process produces low-density foamed products that have a very high quality, with fine cells and without residues coming from the blowing agent. However, the control of foam density is complicated in this type of process.[7] In addition, the investments are high due to the requirement of large high-pressure vessels and the cycle time to produce the foams is also very high.

Compression molding is a versatile process suitable for a wide variety of thermoplastic polymeric matrices. Two different variations are commonly used at industrial level.[4,5,8,9] The single stage process involves two steps, first compounding the polymer

with the blowing agent and all the required additives, (using an extruder or a Bambury type mixer) and second, the foamable compound is placed in a mold and subjected to a high mechanical pressure and to a temperature higher than the decomposition temperature of the blowing agent. Once the entire blowing agent has been decomposed, pressure is released and expansion takes place. The main advantage of the single-stage variation is its simplicity; however it presents several disadvantages being the most important the difficulty of controlling the final foam density. In addition when using low-melt strength thermoplastics, or when high expansion ratios are required, it is necessary to crosslink (either chemically or by irradiation) the polymer to bear the extensional forces occurring during expansion, thus avoiding premature collapse of the foam or the presence of a high number of broken cell walls.[4]

Using the single stage process, densities lower than 70 kg/m^3 are difficult to achieve. To obtain lower densities, a second variation known as two-stage compression molding is used.[5] In this process, expansion takes place in two steps and this, together with the crosslinking of the polymeric matrix, allows lowering the density of the foamed products to values as low as 20 kg/m^3. Second expansion takes place at atmospheric pressure in a mold having the desired size and shape.

Compression molding, either the single or the two-stage variation, present several drawbacks. In the single-stage process, the control of density is made by means of the blowing agent concentration, crosslinking agent concentration, pressure and temperature, and in general is not very accurate.[4] In the two-stage process, the control of density is much accurate however, the foam blocks produced by this method are non-homogenous, with density and cellular structure varying along the block thickness, (cells are smaller close to the surface of the blocks and density is higher in this zone).[10–14] In addition, in both processes the crosslinking of the polymer matrix is necessary which harms its recyclability by conventional re-melting techniques.[15]

The Improved Compression Molding Route, (ICM) can be considered as an alternative foaming route to provide a solution to the aforementioned drawbacks. Its main feature is the use of self-expandable molds that allow controlling the final expansion ratio by mechanical means and obtaining non-crosslinked net-shaped foamed parts in a relative density range between 0.1 and 0.9. These molds have the ability of applying pressure to the polymer while the blowing agent is being decomposed, which allows dissolving the gases generated into the polymer prior to the pressure release and final expansion. In addition, as the molds are capable of controlling the expansion degree it is possible to regulate in a very accurate way both the size and the shape of the foamed part. Moreover, the mold can be designed and produced with different geometries depending on the final application of the foamed part.

The ICM foaming route permits an excellent control of the cellular structure by properly handling temperature and pressure during the process and the chemical composition of the sample in terms of blowing agent content. The cellular structure, with regards to cell size, type, and shape, can be tailored to the final application and hence, it is possible to produce customized foams with similar densities but with significantly different cellular structures. For example, for structural purposes samples with a good mechanical response (i.e. with an almost zero open cell content) are desirable, while for sound absorption applications a high degree of interconnection between the cells is preferred. The ability of this technique to produce foams with different cellular morphologies will be proved in the experimental part of this article.

Even though the independent control of density and microstructure is probably the main characteristic of the ICM there are others that should also be taken into consideration. Any thermoplastic polymer or thermoplastic based composite or nanocomposite can be foamed by this process without the necessity of crosslinking the polymeric matrix. Up to now, pure polymers such as LDPE or EVA, composites such as LDPE/ATH, EVA/ATH, blends of EVA and starch, and nanocomposites based on LDPE and silica nanoparticles have been successfully foamed using the ICM process.[16–23]

Therefore, this article is focused on the analysis of the relationship between the ICM route and the structure and properties of polymeric foams produced by this process. For this purpose, a collection of polypropylene foams with relative densities in the range between 0.3 and 0.6 and with different chemical compositions have been prepared using such process. Foamed discs and cylinders were prepared using a polypropylene matrix.

MATERIALS

A linear random polypropylene copolymer, (200CA10 from Inneos) with a melt flow index of 10 g/min, (measured at 230°C and 2.16 kg) was used to produce all the analyzed samples. Its melting point is 150.4°C and its crystallinity degree is 44.4%, (both were measured by DSC). Azodicarbonamide (Porofor ADC/M-C1 from Lanxess) with an average particle size of (3.9 ± 0.6) μm was used as blowing agent. In order to prevent thermal oxidation of the polymer a small amount of a commercial antioxidant, (Irganox B561 from Ciba) was used in all formulations. Stearic acid (Stearic acid 301 from Renichem) was used as processing aid.

FOAMING PROCESS

As it was mentioned in the introduction, polypropylene foams have been produced using the improved compression molding process (ICM). It comprises the following three steps:

1. Melt-Compounding of Raw Materials: Polymer, blowing agent, the antioxidant, and the processing aid were melt-mixed in a twin screw extruder (Collin mod ZK25T). The temperature profile was varied from 135°C in the hopper to 155°C in the die. Such profile was chosen in order to avoid premature decomposition of the blowing agent during the compounding steps. The material was water cooled and pelletized.Pellets with four different blowing agent concentrations namely 1, 5, 10, and 15 wt % were prepared. Varying blowing agent concentration will permit gaining knowledge

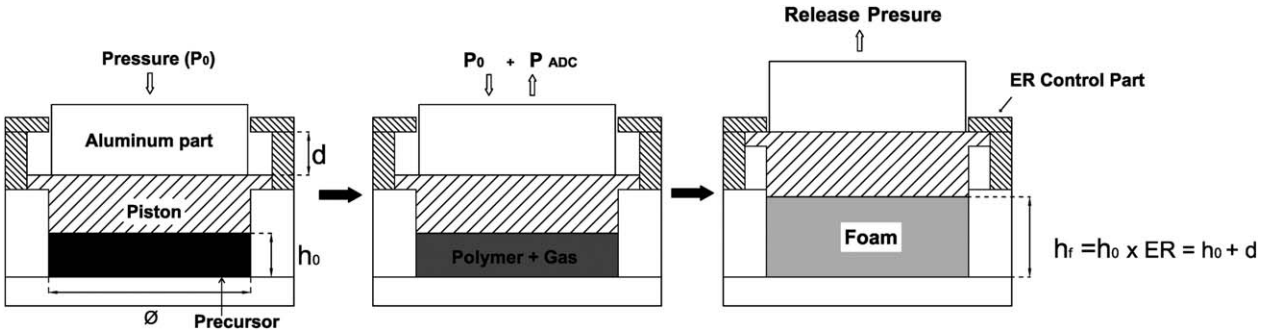

Figure 1. Schematic draw of one self-expandable mold used to produce polypropylene foams via the improved compression molding route.

on the relationship between chemical composition, processing parameters, and cellular structure.

2. Production of Solid Precursors: The second step comprises the fabrication of solid foamable precursors using the previously obtained pellets. Solid cylinders with 20 mm in diameter and 15 mm in height, and discs with 150 mm in diameter and 2 mm in thickness were produced using stainless steel molds and a hot plates press. In both cases the temperature of the press was fixed at 175°C (lower than the decomposition temperature of the azodicarbonamide (ADC) which is in the range between 200 and 220°C).[24] The applied pressure (P_0) was 95 MPa for cylinders and 5 MPa for discs. Pressure and temperature were applied simultaneously for 15 min. Those values were chosen in order to assure a proper densification of the pellets.
3. Foaming Step: The aforementioned thermoformed precursors were introduced in a self-expandable mold with the ability of controlling the expansion ratio of the material. The ICM route can be carried out by using directly as solid precursors the pellets obtained after the melt-compounding process. Nevertheless, in this work thermoformed solid precursors were preferred because they allowed measuring the mechanical properties of the solid materials prior to the foaming step.

Figure 1 shows a schematic draw where it is represented the evolution of both sample and mold during a typical foaming experiment.

In the first stage, the solid thermoformed precursor (or equivalent mass of pellets) is introduced in the mold and an initial pressure (P_0) and foaming temperature (T_F) are applied. The cavity where the precursor is introduced has a defined initial height (h_0). The gas generated starts to be dissolved in the polymer as the blowing agent decomposes (second step) and the pressure increases above P_0. After a certain time (t_F), the pressure is stabilized at a certain value (P_F). This pressure denotes the moment in which the entire blowing agent has been decomposed and then, pressure is released (third step) allowing the piston to displace vertically by the expansion of the polymer inside the mold. The distance covered by the piston is defined taking into account the desired expansion ratio ($ER = h_f/h_0$). Therefore, the final height of the sample is defined as follows:

$$h_f = h_0 + d \quad (1)$$

The movement of the piston is restricted to such distance (d) by the part named "*ER Control Part*". Such parts are interchangeable depending on the desired expansion ratio. Finally, the mold is rapidly introduced in a tank containing cool water to stabilize the cellular structure.

One of the main differences between the ICM route and the conventional one-step compression molding lies in the pressure applied to the foam during foam growing. This difference promotes significant advantages of the ICM process over the conventional compression molding process. On the one hand, the possibility of achieving an accurate control of foam density and on the other hand, the possibility of modifying the microstructure of the foamed part, (in terms of cell size, cell type and cell shape) by acting on both foaming parameters and chemical composition.

The different foaming parameters mentioned, this is t_F, P_0, and T_F are chosen depending on the polymeric matrix type, chemical composition (blowing agent concentration), and sample geometry. In this work, an initial pressure (P_0) of 100 MPa for cylinders and of 4 MPa for discs was applied to the mold. Foaming temperature (T_F) in both cases was 205°C and P_F varied depending on both geometry and azodicarbonamide concentration. Foamed discs and cylinders with the four aforementioned ADC concentrations have been prepared. Samples were expanded to three different expansion ratios (ER) 1.6, 2, and 3 which correspond to nominal densities of 562.5, 450, and 300 kg/m^3, (i.e. relative densities of around 0.6, 0.4, and 0.3 respectively). Samples denomination is as follows, a capital C (for cylinders) or a capital D (for discs) followed by two numbers, the first one indicates the ADC concentration (1, 5, 10 or 15) and the second one, the expansion ratio (1 for 1.6, 2 or 3).

CHARACTERIZATION

Density

Density measurement of both solid precursors and foams was performed by the geometric method; this is by dividing the weight of each specimen between its corresponding volume (ASTM Standard D1622-08). The relative density was calculated as the density of the foams divided by the density of the solid precursor from which the foam was produced

Microstructural Characterization

Cellular structure of both foamed discs and cylinders was analyzed by using scanning electron microscopy (SEM). In order to keep the microstructure, samples were frozen in liquid nitrogen and afterwards fractured. Surface fracture was made conductive

by sputtering deposition of a thin layer of gold and observed using a Jeol JSM-820 SEM. Cell diameter as well as cell density were measured using an image processing tool based on the software Image J.[25] The samples were always taken from the central part of the cylindrical samples.

Open Cell Content

The analysis of the open cell content of foamed samples is essential to understand their mechanical response. In addition, is very useful to be able to determine if they could be potentially used as sound absorbers. In this study, the percentage of open cells (C) was measured with an Eijkelkamp 08.06 Lange air pycnometer according to ASTM D6226-10. The eq. (2) was used according to the ASTM standard:

$$C = \frac{V_{Sample} - V_{Pycnometer}}{V_{Sample} \cdot p} \quad (2)$$

where the geometrical volume, V_{Sample} (calculated from the specimen dimensions), is subtracted from the total volume measured with the pycnometer, $V_{Pycnometer}$, and divided by the volume of air contained in the sample, ($V_{Sample} \cdot p$), where p is the sample porosity calculated by: 1-(ρ_f/ρ_s); ρ_f is the foam density and ρ_S is the density of the polymeric matrix, in this case polypropylene (900 kg/m^3).

Mechanical Response

Mechanical response of foamed polypropylene was measured under different conditions, thus, compression, tensile and bending, tests were carried out. In addition, the solid precursor materials (polypropylene with different ADC contents) were also characterized.

Compression tests were performed in the solid and foamed cylinders using a universal testing machine (Instron model 5500R6025). Experiments were performed at room temperature and at a crosshead rate of 10s^{-1}. The maximum static strain was 75% for all the experiments. Elastic modulus and collapse stress were determined from the stress–strain curves.

Tensile tests were also performed using an Instron 5500R6025, in accordance with ISO 527, at a strain rate of 20 mm/min. Type 1A specimens were machined from foamed and un-foamed discs and five replicates for each material were performed in order to ensure the reproducibility of the results. Elastic modulus and yield strength were determined from tensile tests.

Flexural tests were performed using the same universal testing machine and in accordance with ISO 178 at a strain rate of 5 mm/min. Flexural modulus as well as flexural strength was calculated from the resulting curves.

In all cases, samples were tested under controlled conditions of 23°C and a 50% of relative humidity.

Further information about testing procedure can be found elsewhere.[26–30]

RESULTS AND DISCUSSION

Foaming Process

The hot-plates press in which the foaming experiments were conducted is equipped with a sensor able to measure the pressure during the experiments. Figure 2 shows an example of how pressure evolves with time (a) for a foamed disc and (b) for a foamed cylinder.

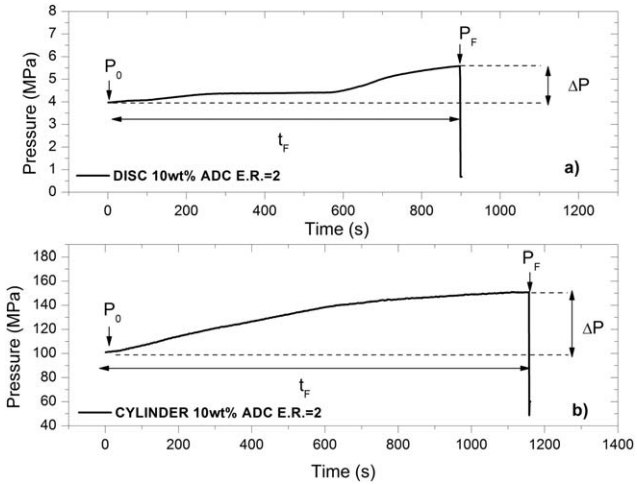

Figure 2. Curves showing the evolution of pressure with time during foaming experiments corresponding (a) to discs and (b) cylinders.

In both cases, the pressure (b) increases as the experiment progresses. However, there are some differences between both types of samples. While for cylinders the increase is produced from the very beginning of the experiment, for discs this increase takes a longer time. This difference is related with the different size of both molds. The mold used for disc is much bigger and then requires longer time to warm and to reach the melting temperature and the decomposition point of the ADC and then to increase the pressure.

There are other differences related with the total increment of pressure ($\Delta P = P_F - P_0$) and foaming time (T_F). Figure 3(a,b) summarize the average values of T_F for discs and cylinders respectively. Foaming time is slightly shorter for discs than for cylinders. Although the mold is bigger for discs, cylinders are thicker than discs (20 and 2 mm respectively) and hence they need a slight longer time for the ADC to be fully decomposed. Moreover, T_F remains approximately constant for each type of samples (discs or cylinders) being not possible to observe any trend with density or with ADC concentration.

Pressure increment (ΔP) has been calculated for the whole collection of samples and values are plotted as a function of ADC content in Figure 3(c) (discs) and Figure 3(d) (cylinders). For discs, ΔP increases linearly as ADC concentration does however, for cylinders this trend is not maintained. In addition, the values of ΔP reached by either discs or cylinders are significantly different, a maximum of 2 MPa for discs and a maximum of around 120 MPa for cylinders.

As very different initial pressures were applied to these geometries, (4 MPa for discs and 100 MPa for cylinders), the evolution of the pressure during foaming could be also different. It seems that the much higher applied pressure in cylinders hinders the real effect of ADC decomposition, leading to not linear trends between pressures and blowing agent concentration.

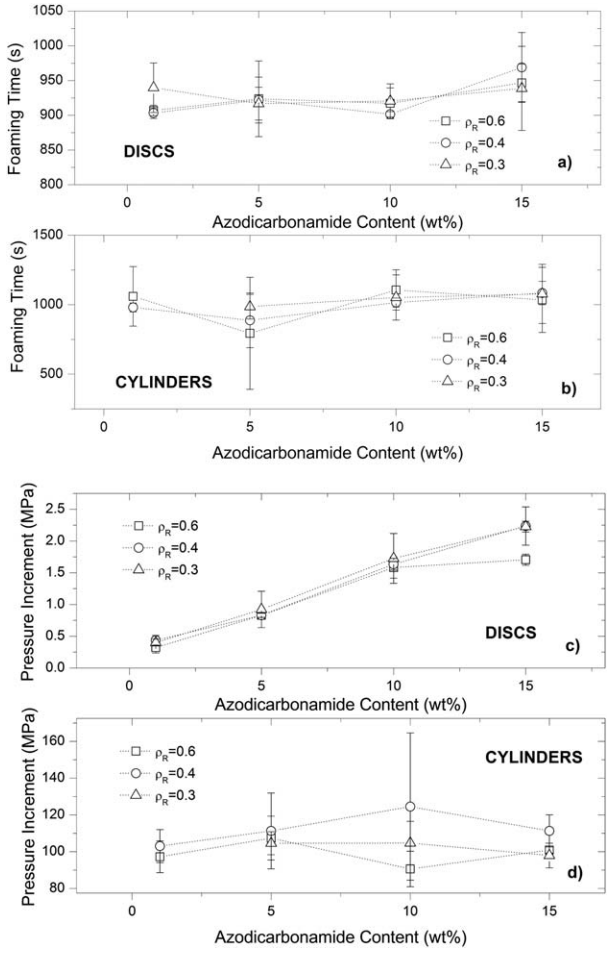

Figure 3. Average values of foaming time for PP foams ((a) discs, (b) cylinders) and average values of pressure increment ((c) discs, (d) cylinders).

It was said in the introduction that one of the main advantages of the ICM route with respect to the conventional one is the accurate control of foam density that can be achieved. Table I summarizes average density values of both foamed discs and cylinders and their respective relative densities. In addition, the coefficient of variation (CV) calculated as the ratio between the density and the standard deviation is also presented in this table. These values were calculated using the density and standard deviation values of five different samples of each type. These values provide information about the accuracy and repeatability of the process.

The results indicate that a higher degree of repeatability is reached for discs than for cylinders because the average CV for the disc samples is lower (0.028) than that of the cylinder samples (0.045); the high pressures applied to the latter type of samples during the foaming step can produce small leakages of polymers out of the mold leading to samples with densities different than the nominal one.

Table I is also includes other parameter that has been called % Deviation *(%D)* which measures the deviation of the foam density from the expected nominal density. It has been calculated using eq. (3).

$$\%D = \frac{\rho_{Real} - \rho_{Nominal}}{\rho_{Nominal}} \times 100 \quad (3)$$

where ρ_{Real} is the measured density of the samples and $\rho_{Nominal}$ corresponds to expected nominal densities for the three considered expansion ratio (i.e. 562.5 kg/m^3 for ER=1.6, 450 kg/m^3 for ER=2, and 300 kg/m^3 for ER=3). When $\%D$ is negative it means that the experimental value is lower than the expected one and when it reaches positive values, it means that experimental value is higher than nominal one.

Table I. Average Density Values (ρ), Coefficient of Variation (*CV*), Relative Density (ρ_R), and Percentage of Deviation *(% D)* with Respect to the Nominal Density Values (i.e. 562.5, 450, and 300 kg/m^3 for 1, 2, and 3 Samples)

	CYLINDERS						DISCS				
	Sample	ρ (kg/m^3)	CV	ρ_R	%D		Sample	ρ (kg/m^3)	CV	ρ_R	%D
1 wt % ADC	C1-1	525.2	0.046	0.59	−6.61	1 wt % ADC	D1-1	606.2	0.024	0.72	7.78
	C1-2	423.8	0.012	0.48	−3.81		D1-2	459.9	0.043	0.54	2.20
	C1-3	294.0	0.025	0.33	−1.97		D1-3	308.2	0.009	0.35	2.67
5 wt % ADC	C5-1	530.0	0.039	0.58	−5.77	5 wt % ADC	D5-1	541.7	0.022	0.61	−3.68
	C5-2	461.3	0.084	0.49	2.52		D5-2	426.6	0.026	0.48	−5.17
	C5-3	284.0	0.026	0.31	−5.31		D5-3	317.3	0.008	0.38	5.79
10 wt % ADC	C10-1	502.2	0.067	0.57	10.70	10 wt % ADC	D10-1	539.8	0.022	0.62	−4.01
	C10-2	424.5	0.056	0.46	−5.66		D10-2	416.1	0.022	0.45	−7.51
	C10-3	288.3	0.014	0.31	−5.55		D10-3	303.8	0.041	0.34	1.29
15 wt % ADC	C15-1	450.8	0.067	0.48	19.84	15 wt % ADC	D15-1	482.8	0.066	0.55	14.15
	C15-2	387.9	0.094	0.42	13.78		D15-2	382.4	0.005	0.43	15.00
	C15-3	287.9	0.012	0.30	−7.00		D15-3	299.5	0.051	0.33	−0.15

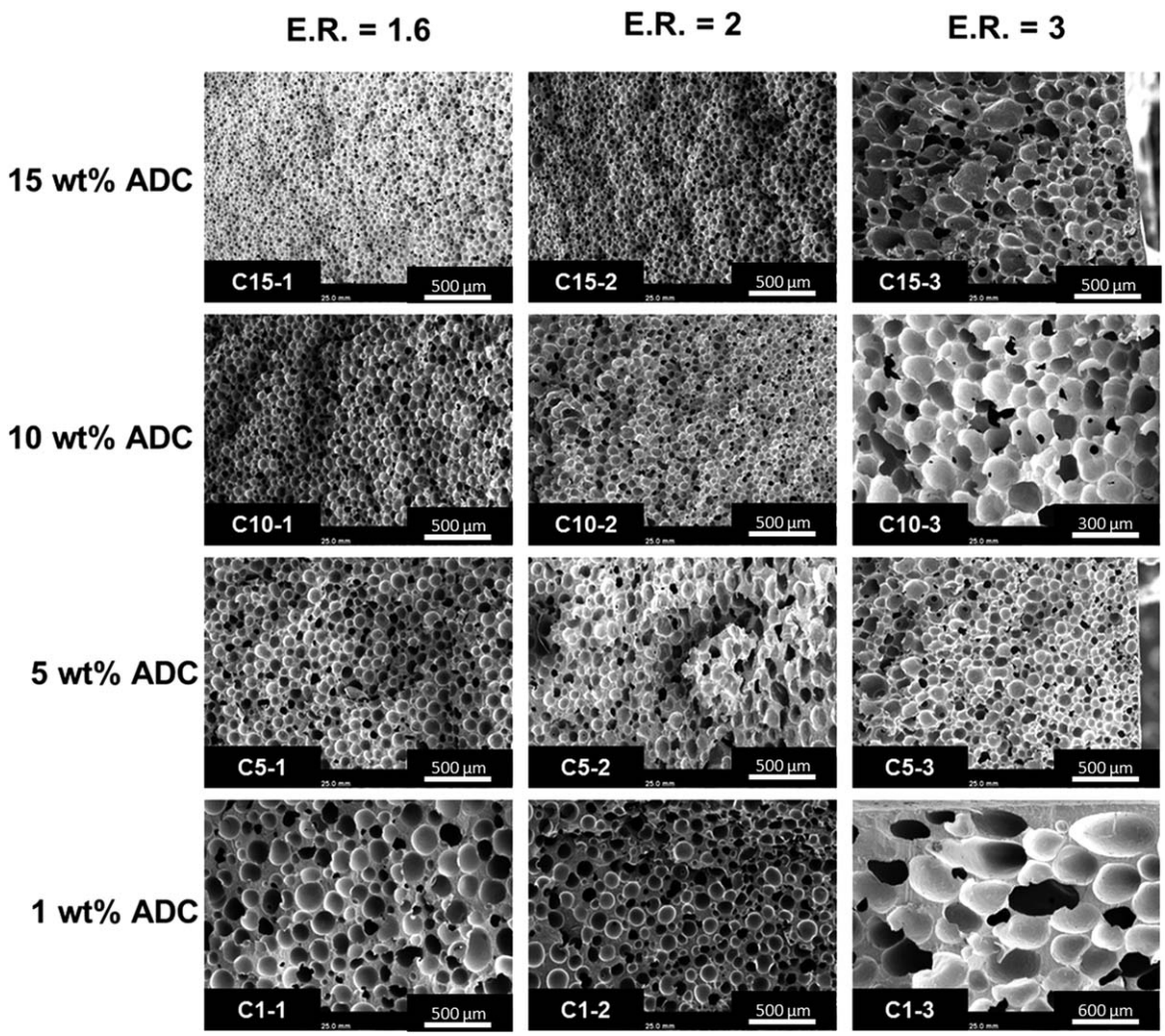

Figure 4. Micrographs corresponding to cylindrical shaped PP foams produced using the ICM route. Note: Images for samples C-10-3 and C-1–3 were taken with a different magnification.

The values in the table indicate that %*D* increases as ADC concentration does and it is higher for cylinders than for discs. As ADC content increases the pressure inside the mold also does and the polymer can easily escape from the mold. Negative values, this is experimental values of density lower than nominal one are in general due to leakages of material out of the mold, either because of high applied pressures, as in the case of cylinders or because the high pressure generated by the decomposition of high amounts of ADC, (samples with 15 wt % of ADC). Positive values of %*D*, this is densities higher than expected ones, can be due to the shrinkage of the foamed product during solidification.

Microstructure

The analysis of the cellular structure of polypropylene foams produced by the improved compression molding route has been focused on cylindrical shaped samples. SEM micrographs showing the cellular structure of foams with different densities and blown using different ADC concentrations are shown in Figure 4.

As it can be observed, as both density or blowing agent concentration are varied a wide collection of different cellular structures can be achieved. Although all the samples exhibit an isotropic cellular structure some differences related with the effect of density and ADC concentration can be inferred from the micrographs. On the one hand, as blowing agent amount increases, cell size decreases and cell density increases and on the other hand, as density decreases cell size increases and cell density decreases. To both quantify and easily understand those effects, cell density and cell size have been measured and the average values of both of them are plotted as a function of ADC content in Figure 5.

As density decreases, cell size increases, being the cell size of samples with the higher relative density around three times lower than that of the samples with the lower relative density. With regard to cell density, it can be observed in Figure 5 that it decreases as density does. As density decreases, the polymer has to expand to higher values and hence, cell walls are thinner and coalescence and/or coarsening phenomena can easily take place.[4]

The variation in ADC concentration also has an important effect on both cell size and cell density. The increment in blowing agent concentration leads to significant cell size reductions,

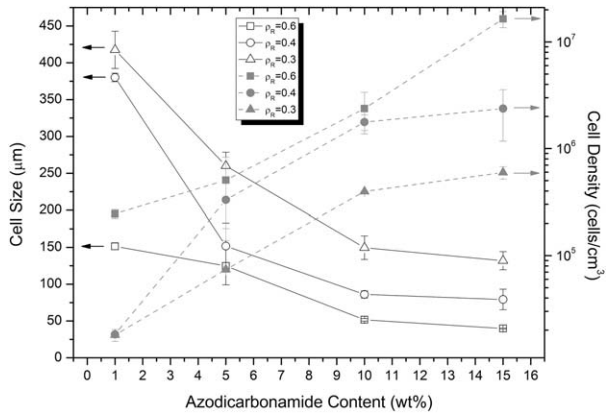

Figure 5. Cell size and cell density of cylindrical shaped polypropylene foams produced using the ICM route.

even reaching values of cell sizes below 100 μm for samples with high ADC concentrations (10 and 15 wt %). Chemical blowing agents such as azodicarbonamide are self-nucleating,[5] so as blowing agent concentration increases the number of available nucleating sites also does, leading to smaller cell sizes and higher cell densities.

Among cell density and cell size other parameters such as the cell size distribution influences the macroscopic response of foamed materials.[2] Typically, histograms of cell size distributions are plotted and afterwards compared, however, due to the high number of samples included in the study the standard deviation of the cell size distribution (*SD*), (accounting for the width of the cell size distribution) has been calculated using eq. (4):

$$SD = \sqrt{\sum_{i=1}^{n} \frac{(\phi_i - \phi)^2}{n}} \tag{4}$$

where n is the number of counted cells, ϕ_i is the cell diameter of cell i and ϕ is the average diameter of the cells. This parameter is a measure of the homogeneity of the cell size distribution.

Results, [Figure 6(a)] clearly indicate that as blowing agent concentration increases, more homogeneous cellular structures are achieved. In addition, it can be observed that samples with relative densities between 0.4 and 0.6 exhibit very similar values of *SD*. For lower densities ($\rho_R = 0.3$) values of *SD* significantly increase. For these samples the polymer is subjected to higher stretching forces that can lead to a higher proliferation of coarsening and/or coalescence phenomena as it was previously mentioned.

Other important parameter to take into account is the open cell content (*C*). It is known that this parameter can have a high influence on the mechanical response of polymeric foams.[2] In addition, for this study a conventional linear PP grade has been used, and hence it is worthy to know how the process itself and the chemical composition of the samples affect the open cell content. Experimental measurements were performed using an air pycnometer and results are plotted as a function of blowing agent concentration in Figure 6(b).

As it can be observed there is a significant difference between samples with relative densities around 0.3 and the rest of samples. For those samples, open cell content remains constant (around a 60%) regardless of the azodicarbonamide concentration used to blown them. Those results indicate that at low densities, open cell content is conditioned mainly by expansion ratio. When the polymer needs to expand to higher ratios, cell walls become thinner and hence cell walls are easily breakable leading to a higher number of interconnections between cells. On the other hand, for samples with relative densities between 0.4 and 0.6 it can be observed how open cell content increases as blowing agent concentration does. In this case, an excess of pressure in the system (due to higher contents of the blowing agent) can break cell walls leading to a higher degree of interconnection between the cells.

Analysis of the Mechanical Response

The analysis of mechanical response has been performed using relative values; this is considering the property of the foam divided by that of the solid. This type of analysis allows analyzing the influence of density and blowing agent amount, and in addition permits accounting for the influence of cellular structure on the mechanical properties. It has been reported by several authors[2,7,10,31–35] that the properties of a cellular polymer can be predicted using the following equation:

$$\frac{P_f}{P_s} = C\left(\frac{\rho_f}{\rho_s}\right)^n \tag{5}$$

where P_f is the property of the foam and P_s is the same property but for the solid polymer, and (ρ_f/ρ_s) is the relative density of the foam. C and n are parameters that can be determined experimentally.

Most foamed products exhibit values of C close to 1 and values of n in a range between 1 and 2. n is closely related with the cellular structure of the foamed product, being closer to 1 for materials with closed cell cellular structures, homogeneous cell size distributions and small cell sizes and it is closer to 2 as open cell content and cellular structure inhomogeneity increase.[2] Hence, eq. (5) allows analyzing in a quite simple way the efficiency of the foaming process in terms of producing low density foams with good mechanical performance.

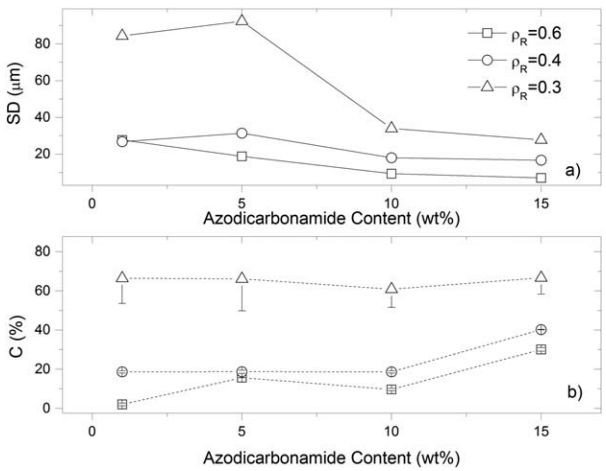

Figure 6. (a) SD coefficient for the analyzed cylinders. (b) Open cell content of cylindrical samples.

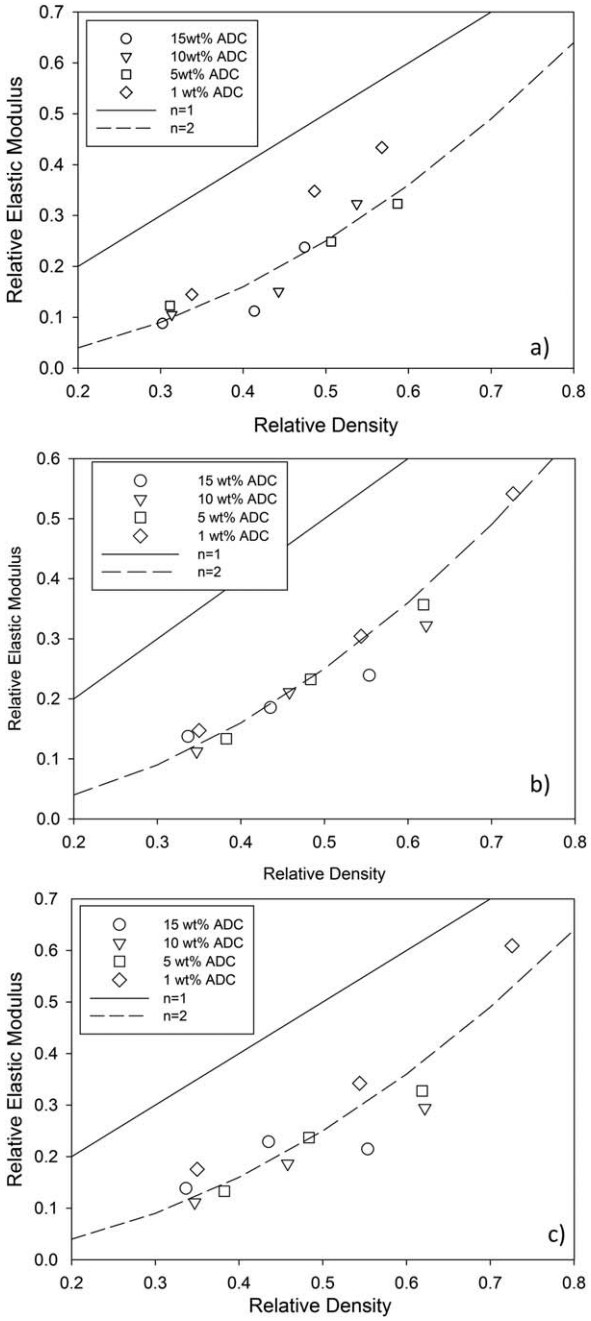

Figure 7. Relative elastic modulus measured in different configurations. (a) Compression. (b) Tensile. (c) Three point bending.

For instance when the aforementioned property is the elastic modulus (E) it can be concluded that for similar values of relative density (ρ_f/ρ_s) the foamed material reaching a value of n closer to 1 will exhibit better specific mechanical properties (higher value of E_f/E_s). As most foams exhibit values of n between 1 and 2, the reduction in mechanical properties is always greater than the corresponding density reduction. This means that the value of n can be considered as an index of under what conditions which of the analyzed foams will have a better mechanical performance.

Figure 7(a–c) shows the relative elastic modulus measured in compression, tensile and bending tests as a function of relative density. n has been calculated considering the relative elastic modulus values measured in different configurations and results are presented in Table II. As it was expected n reaches values between 1 and 2 which is in agreement with the theoretical estimations.

It can be inferred from Figure 7(a) that the cellular structure that maximizes stiffness is the one exhibited by samples blown using 1 wt % of ADC; the value of n obtained for this samples is the closest to 1. So, although those samples presented the highest value of the average cell size, its very low open cell content [close to 0, see Figure 6(b)] lead to better mechanical performance than the ones obtained for samples with lower cell sizes. This means that for the same relative density the role played by open cell content is more significant than the one played by cell size or cell size distribution homogeneity. This result is in concordance with previous studies of our group[7,10] and from other researchers.[33]

When the same type of analysis is performed with the results obtained from tensile tests, [Figure 7(b)] it can be concluded that in this case there is no significant differences between the samples made using different ADC concentrations. In fact, values of n are very similar although for 1 wt % of azodicarbonamide is slightly smaller. It seems that the different types of cellular structures achieved do not have a significant effect on the mechanical response of the samples when they are subjected to uniaxial tensile forces.

Finally, when the results obtained from flexural tests are analyzed [Figure 7(c)] it can be concluded that once more the cellular structure showing the best mechanical performance is obtained using a 1 wt % of azodicarbonamide. In fact the value of n showed by those samples is considerably smaller than that for the other materials. As it was detected for compression tests, open cell content plays a more important role than cell size or cell size distribution in the mechanical response.

If values of n are compared now for the different measurement configurations, analyzed polypropylene foams have a better response in compression or bending than in tension due to the lower value of n.

Besides the analysis of elastic modulus in relative terms, the same type of study can be performed for parameters accounting for the post-elastic behavior, this is, collapse stress, yield stress or flexural strength. Figure 8(a–c) show those three parameters

Table II. Values of n Obtained from the Fitting of Relative Elastic Modulus [Eq. (5)] Calculated for Different Types of Mechanical Tests

n-Elastic modulus	Compression	Tensile	Three-point bending
1 wt % ADC	1.55	1.90	1.67
5 wt % ADC	2.02	2.08	2.14
10 wt % ADC	2.00	2.17	2.32
15 wt % ADC	2.12	2.14	2.10

represented as a function of relative density. In addition, experimental data have been fitted to a power law according to eq. (5). The results obtained for n are shown in these figures and in Table III. As it can be observed, the highest value of n are obtained for collapse stress and yield strength, this is when samples are subjected to uniaxial tensile forces. On the other hand, the closer values to $n = 1$ regardless ADC-concentration are reached by flexural strength. Therefore, results in Table III are indicating that the samples under study have a superior performance in terms of strength when they are subjected to flexural forces.

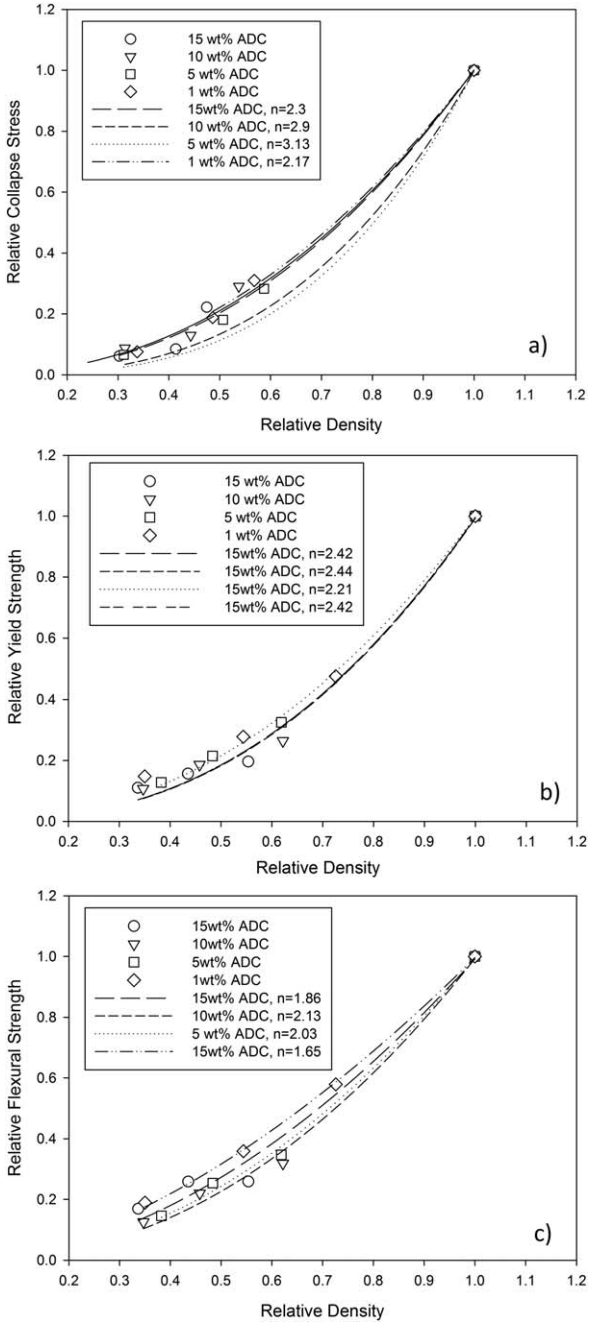

Figure 8. (a) Relative collapse stress. (b) Relative yield strength. (c) Relative flexural strength.

Table III. Values of n Obtained from the Fitting of Collapse Stress, Yield Strength, and Flexural Strength to Eq. (5)

n-Plastic collapse	Collapse stress *compression*	Yield strength *tensile*	Flexural strength *three-point bending*
1 wt % ADC	2.17	2.42	1.65
5 wt % ADC	3.13	2.21	2.13
10 wt % ADC	2.9	2.44	2.03
15 wt % ADC	2.3	2.42	1.86

As it happened for the elastic modulus (Table II), the values of n closer to 1 are always obtained when the smallest amount of azodicarbonamide is used.

CONCLUSIONS

A detailed description of the improved compression molding foaming route has been undertaken along the article. In addition to easily understand all the concepts and parameters involved in the process, a collection of polypropylene foams with relative densities ranging from 0.3 to 0.6 have been produced using such foaming route.

It has been proved that the ICM route is suitable to produce foams from a conventional linear polypropylene without the necessity of crosslinking it, achieving an accurate control of foam density due to the use of special molds and a closed control of both pressure and temperature. In addition, it has been detected that a good accuracy in the foam density can be achieved using lower initial pressures and/or lower blowing agent concentrations.

A proper set of foaming parameters together with the variation of chemical compositions (by means of using different blowing agent concentrations) can lead to a wide variety of cellular structures in terms of cell sizes, cell size homogeneity or open cell content. It was found that using high initial pressures and high ADC concentrations, cellular structures with cell sizes below 100 μm and with a very narrow cell size distribution can be achieved. As density is lowered, the polymer is expanded to higher ratios and as a consequence the open cell content reached values of 60%. Mechanical response of the foams has been determined using different measuring configurations. The analysis of mechanical properties in terms of relative values has been used to understand the influence of microstructure on mechanical behavior. The results, (regardless of measurement configuration) show that the cellular structure maximizing mechanical response is the one with the almost-zero open cell content which is presented by samples produced using the smallest amount of azodicarbonamide. So, for the same density values, these results indicate that cell size plays a secondary role when it is compared to open cell content, because samples with more homogeneous cell size distributions and very fine cell sizes but with higher open cell contents have a poorer mechanical performance. Regarding the general behavior of the analyzed materials and taking into account the values of n parameter, it

can be said that they behave better in compression and bending and slightly worse in tension.

As a general conclusion it can be said that the ICM route is a suitable foaming process to produce non-crosslinked net-shaped foams that can be applied to a wide variety of thermoplastic polymeric matrices. The accurate control of density, together with the possibility of achieving different types of cellular structures is the main characteristics of this process.

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