SYNTACTIC & COMPOSITE FOAMS

Moulded polypropylene foams produced using chemical or physical blowing agents: structure–properties relationship

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Abstract Polypropylene (PP) foams have become essential items due to their excellent properties. Nevertheless, obtaining net-shaped PP foams with medium relative densities is a complicated issue. In this article, two processes able to produce moulded PP foams in this density range are presented. One of them is based on a modification of the pressure quench foaming method and therefore uses a physical blowing agent (CO_2). The second one is the improved compression moulding technique which uses a chemical blowing agent (azodicarbonamide). PP foams with relative densities in the range between 0.25 and 0.6 and cylindrical shape were prepared using these foaming techniques. A common PP grade (instead a highly branched one) was used to obtain the samples, showing, that by combining the appropriate foaming technique, the adequate moulds, suitable blowing agent and proper foaming parameters, net-shaped PP foams with excellent properties can be produced starting from a conventional PP grade. Samples were characterized by analyzing their cellular structure and their mechanical properties. Results have showed that depending on the chosen foaming route isotropic or anisotropic structures with cell sizes ranging from 40 to 350 μm and open cell content in the range between 0 and 65% can be obtained. Moreover, mechanical properties are highly influenced by the production route and chemical composition of the foams. For instance, the stiffer materials at relative densities higher than 0.4 are the ones produced using the chemical blowing agent while at relative densities lower than 0.4 are the ones produced using the physical blowing agent.

Introduction

Polymeric foams can be defined as two-phase materials in which a gas is dispersed in a continuous macromolecular phase [1–3]. Foams, owing to the combination of excellent properties and costs savings have found an application in almost every field [2, 3].

Polypropylene (PP) is a commodity polymer that due to its outstanding functional characteristics and low material costs has been considered as a substitute for other thermoplastic polymers [4]. However, foaming PP is not a simple task [5–7] mainly due to two reasons; first, PP is a semicrystalline polymer, and as it is known that gases do not dissolve in crystalline regions. This hinders obtaining a homogeneous polymer/gas solution in solid state and hence controlling foaming process is much more difficult than for amorphous polymers when the solid state foaming process is used [8]. The second reason lies in the weak melt strength exhibited by PP. Low melt strength leads to a rupture of the cell walls under the elongational forces occurring during cell growth; as a result, final foam has a high amount of coalesced and open cells which harms their mechanical properties and makes it unsuitable for many applications [8, 9].

The main solutions proposed up to now are based in increasing melt strength of the polymer through different

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ways. On the one hand, by filling PP with inorganic compounds such as talc or nanoparticles [10–12] and on the other hand by using special PP grades known as high melt strength PPs, on which by promoting a high degree of branching the melt strength is significantly increased [6, 11, 13]. Finally the less desirable solution because turn the polymer non-recyclable, is crosslinking the PP matrix [1].

Regardless the aforementioned handicaps, both linear and highly branched PP grades have been foamed with more or less success using different foaming processes such as extrusion, compression moulding, injection moulding or batch foaming [2, 3, 5–11]. Nonetheless, when the final application of the foamed part requires a certain final shape, the number of suitable foaming processes becomes limited.

In the literature it is possible to find examples of extruded PP foams; they can be classified in two types, low density foamed sheets [2, 3] or foamed filaments, [6, 7, 9–11]. Low density extruded sheets can be shaped by thermoforming but the need for a secondary process can contribute to increase the cost of the final part and thermoforming is only limited to simple shapes. Extruded filaments are made using the process developed by Park and co-workers [6, 7, 9–11] which is based on obtaining fine celled PP foams in a wide range of relative densities (between 0.1 and 0.9). For this purpose they use high melt strength PP grades or add fillers to the base PP. Regarding to the shape, they used to work with a filamentary die with a very small diameter (around 0.45 mm [6]), so that the obtained foam is only suitable for scientific purposes.

Xu [8], Jian [14], Zhai [15] and their respective co-workers have proved that despite its semicrystalline character, PP pellets or very thin sheets (50 μm thickness) can be foamed by gas dissolution using supercritical CO_2 as blowing agent. Nevertheless, all those works only deal with the structural characterization of the foamed samples. Results regarding mechanical or thermal properties of the foams are not provided. The limitations imposed by the non-regular shape and small size of so-obtained PP foams have resulted in a lack of information about the influence of foaming parameters in the structure–properties relationship. Thus, although very good cellular structures (in terms of cell size and homogeneity) are obtained by using gas dissolution as foaming process [8, 14] it is unknown its influence on the physical response of PP foams.

Taking into account the previous facts, it seems that nowadays the most suitable foaming process to obtain moulded PP foams is injection moulding. It is possible to use a conventional injection moulding machine with small modifications and physical or chemical blowing agents to produce PP foamed parts. Although foaming injection moulding offers several advantages such as the absence of sink marks on the final part surface, reduced weight, lower back pressure, faster production cycle or higher stiffness to weight ratio there are also several disadvantages. Maximum weight reduction is limited to a 40%, samples have a wide distribution of cell sizes what can negatively affect to their properties, and moreover, the quality of foamed part surface is not as good as for solid parts [16–19].

During the last years efforts have been focused in microcellular injection moulding process, also known as Mucell process [20]. It allows producing microcellular foams but weight reduction is limited to around a 25% and it is not suitable for producing big parts. Thus, it seems that injection moulding is adequate to produce moulded foams but with the main disadvantage that operating density range is very limited (usually relative density values higher than 0.6).

The main objectives of this article are connected with some of the previous topics in which a lack of knowledge has been detected in the literature. So, the first goal is to produce shaped PP parts with medium relative densities (between 0.25 and 0.6). To cover this objective, two different foaming methods have been used, a modified pressure quench method and the improved compression moulding technique.

The second goal is to gain knowledge on the structure–property relationships for these materials. As the produced samples have a cylindrical geometry with a significant thickness, it has been possible to measure the mechanical properties analyzing them as a function of the foams structure. A comparative study of the materials produced from both methods is also presented.

Finally, the third objective is to analyze if by using adequate formulations and processing parameters it is possible to produce foamed parts with relative densities in the range 0.2–0.6 with a good quality using a conventional linear non-filled PP avoiding the use of high melt strength PPs.

Materials and foaming processes

Materials

A random PP 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 chemical blowing agent and CO_2 with a high purity was used as physical blowing agent. In order to prevent thermal oxidation of the polymer a commercial antioxidant (Irganox B561 from Ciba) was added. Stearic acid (Stearic Acid 60/40 from Renichem) was used as processing aid.

Foaming processes

Modified pressure quench method

In a first step, PP pellets were re-extruded in a twin-screw extruder (Collin Kneter 25X36D) at a rotating speed of 160 rpm and with a temperature profile varying from 130 °C in the hopper to 155 °C in the die. Extruded material was water cooled and pelletized. A 0.1 wt% of both antioxidant and processing aid (stearic acid) were added to the polymer.

In a second step, discs with 20 mm in diameter and 3 mm thickness were compression moulded in a two hot-plates press at 170 °C and 40 bars. The so-obtained discs are placed in a mould which is at the same time disposed inside a high pressure vessel.

This mould has the ability of controlling the final density of the foams as well as allows producing a shaped foamed part (cylindrical in this paper, although other geometries could be produced using the same process). Figure 1 shows a schematic draw of such mould. As it can be observed, it is a cylindrical mould with an internal cavity of 20 mm in diameter and 12 mm in height made of stainless steel. There are also several cylindrical inserts with different heights but with the same diameter of the cavity (20 mm). Those inserts allow reducing the volume of the mould internal cavity to increase the foam density.

To control the density of the foam, the volume of the precursor (solid PP discs), is kept constant while the volume of the cavity of the mould is varied using the previously mentioned inserts. So, precursors always have the same weight and dimensions but they are expanded to
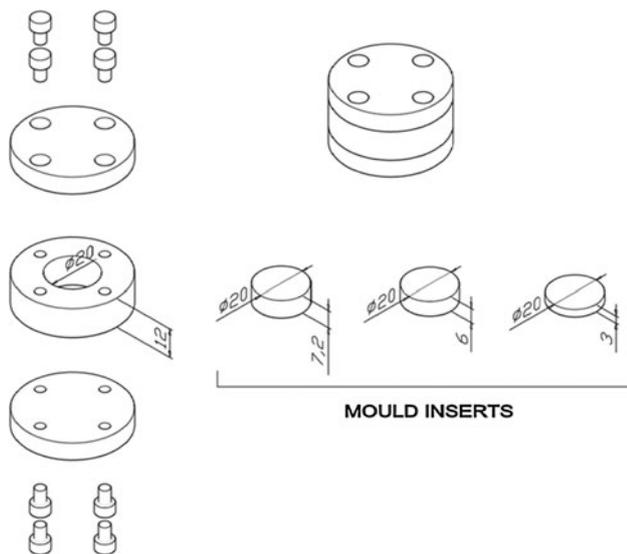
Fig. 1 Schematic draw of the mould use to produce foams by the modified pressure quench method

different heights which are controlled by the height of mould cavity.

It has been possible to obtain foams with expansion ratios of 1.6, 2, 3 and 4, which corresponds to nominal densities of 562.5, 450, 300 and 225 kg/m³. The use of a mould inside the pressure vessel to produce net-shape parts is not a common practice, although as it is shown in this paper is a promising technique.

As it was previously mentioned, samples were produced by the pressure quench method. This method comprises two steps. First, a thermoplastic sample is placed in a high pressure vessel and saturated with an inert gas, typically CO_2 in the supercritical region. For an amorphous polymer gas saturation is performed at a temperature slightly below its glass transition temperature, while for semicrystalline polymers, in order to increase gas sorption it is done at a temperature slightly above its melting point. Then, upon a prolonged exposure to supercritical CO_2 at high pressure a polymer/gas solution is formed. In a second step, the system is rapidly depressurized. The rapid pressure quench decreases the gas solubility in the polymer and causes bubble nucleation due to supersaturation.

In this study, PP discs placed inside the mould were saturated with CO_2 at different pressures varying from 170 to 240 bar. Saturation pressure was chosen depending on the final density of the sample; as density should be lower, saturation pressure was higher. Gas dissolution step was performed at a constant temperature of 155 °C. After 40 min, polymer/gas solution was cooled down until foaming temperature. Then, samples were foamed by rapid depressurization of the autoclave. Sample density (expansion ratio) was controlled with the mould dimensions, pressure drop (ΔP) and foaming temperature. In addition, along the experiments, final pressure (remnant pressure in the autoclave after depressurization step) was also tuned to have a more accurate control of the expansion degree of the sample.

Table 1 shows the main processing parameters used to produce foams with the four different density values allowed by the mould. Saturation temperature was kept constant along the experiments while saturation pressure, foaming temperature and pressure drop were adjusted for each expansion ratio value. It can be also observed that both saturation pressure and pressure drop were increased as density decreases.

It can be also concluded from Table 1, that as density decreases, residual pressure inside the autoclave after depressurization was lower. In fact, for the lightest materials, the autoclave remains open after depressurization to assure the complete expansion of the samples. Regarding to foaming temperature, it can be seen how as expansion ratio increases, foaming was performed at lower temperatures. As the density decreases the base polymer is stretched to

Table 1 Foaming conditions used to produce moulded polypropylene foams using CO_2 as blowing agent

Sample	$\rho_{Theoretical}$ (kg/m^3)	$T_{Saturation}$ (°C)	$t_{Saturation}$ (min)	$P_{Saturation}$ (bar)	$T_{Foaming}$ (°C)	$P_{Foaming}$ (bar)	Pressure drop (ΔP, bar)	Final pressure (bar)
D1	562.5	155	40	185	125	155	100	55
D2	450	155	40	200	125	170	120	50
D3	300	155	40	235	120	180	160	20
D4	225	155	40	240	115	190	190	0—Open

higher ratios and hence it is necessary to increase the melt strength of the polymer by decreasing foaming temperature. Moreover, it should be taken into account that at high pressures, gas concentration is higher leading to lower viscosities and therefore reducing temperature is needed to increase polymer viscosity.

Designation of CO_2 blown samples will be as follows. A D followed by a number that indicates expansion ratio value, so samples will be named as D1 (for expansion ratio of 1.6), D2, D3 and D4.

Table 2 summarizes the expected values of density, real density, relative density, and theoretical and real expansion values. Comparing expected and obtained values of both density and expansion ratio, it can be concluded that foaming parameters were suitably chosen and an accurate control of foaming process was achieved.

Improved compression moulding

In this foaming route, the first step comprises melt compounding of raw materials. Thus, PP, blowing agent (azodicarbonamide), stearic acid and antioxidant were melt-mixed in a twin-screw extruder (Collin Kneter 25X36D) with a temperature profile varying from 130 °C in the hoper to 155 °C in the die and at a rotation speed of 160 rpm. Material was water cooled and pelletized.

Pellets with different blowing agent contents (1, 5, 10 and 15 wt%) were produced. The use of different contents of azodicarbonamide was aimed to analyze the effect of blowing agent amount in both cellular structure and mechanical properties of so-produced foams.

The second step comprises the preparation of precursor materials which in this case are cylinders with 20 mm in diameter and 15 mm in height. They were produced using a cylindrical shaped mould and a two hot-plates press at a temperature of 175 °C and using a pressure of 3 Tn during 10 min.

Foaming step was conducted under mechanical pressure using the so-called self-expandable moulds. Those moulds allow controlling density of the foamed sample. A temperature of 205 °C and an initial pressure of 95 MPa were used to produce foams with different azodicarbonamide contents. A more detailed description of this foaming process can be found elsewhere [21–23].

For azodicarbonamide blown samples, designation is as described. An A followed by two numbers, first one indicates azodicarbonamide amount (1, 5, 10 or 15 wt%) and second one the expansion ratio value (1 for 1.6, 2 and 3). For example sample A-5-2 was foamed using a 5 wt% of azodicarbonamide and an expansion ratio of 2.

Foams with expansion ratios of 1.6, 2 and 3 were produced using this method. Average density and relative density values of so-produced foams are summarized in Table 3.

Experimental

Density

Density measurements of both precursors and foamed samples were performed by the geometric method; this is by dividing the weight of each specimen between its corresponding volume (ASTM standard D1622-08).

Structural characterization

Cell morphology of the samples was analyzed by using scanning electron microscopy. Samples were frozen with liquid nitrogen and fractured. Fractured surface of the samples was made conductive by sputtering deposition of gold and observed using a Jeol JSM-820 scanning electron microscope. Average cell diameter and cell density were determined using an image processing tool based on the software ImageJ [24]. In addition, anisotropy ratio (R) which can be defined as the ratio of the mean intercept

Table 2 Values of density, relative density and expansion ratio (E.R. $= \frac{\rho_{Solid}}{\rho_{Foam}}$) of moulded polypropylene foams

Sample	ρ_{REAL} (kg/m^3)	$\rho_{RELATIVE}$ (kg/m^3)	E.R. (Theoretical)	E.R (Real)
D1	534.8 ± 33.5	0.594	1.6	1.69 ± 0.09
D2	447.9 ± 17.5	0.497	2	2.01 ± 0.07
D3	290.4 ± 5.4	0.322	3	3.10 ± 0.05
D4	218.5 ± 2.8	0.242	4	4.12 ± 0.05

Table 3 Main characteristics of foams produced by the improved compression moulding route using azodicarbonamide as blowing agent: density, relative density and real expansion ratio (theoretical expansion ratios were 1.6, 2 and 3)

Sample	ρ (kg/m^3)	ρ_R	E.R.$_{REAL}$
1 wt% Azodicarbonamide			
A1-1	525.7	0.595	1.60
A1-2	432.2	0.483	1.97
A1-3	294.1	0.337	3.01
5 wt% Azodicarbonamide			
A5-1	512.5	0.571	1.61
A5-2	444.2	0.498	1.98
A5-3	279.2	0.313	3.04
10 wt% Azodicarbonamide			
A10-1	474.0	0.525	1.71
A10-2	424.5	0.456	2.01
A10-3	281.8	0.307	3.01
15 wt% Azodicarbonamide			
A15-1	436.8	0.469	1.73
A15-2	387.9	0.420	2.01
A15-3	287.9	0.306	3.08

length in the longitudinal direction to that in the perpendicular plane [25] was also measured using the aforementioned software

Open cell content

The percentage of open cells (C) was measured with an Eijkelkamp 08.06 Lange air pycnometer according to ASTM D6226-10. The following equation (1) was used according to the ASTM standard:

$$C = \frac{V_{Sample} - V_{Pycnometer}}{V_{Sample} \cdot p} \qquad (1)$$

where the geometrical volume, V_{Sample} (calculated from the specimen dimensions) is subtracted from the sample 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 $\left(1 - \frac{\rho_f}{\rho_S}\right)$; ρ_f is the foam density and ρ_S is the density of the polymeric matrix, in this case PP ($\rho_S = 900$ kg/m^3)

Mechanical tests

Mechanical response of solid precursors and foamed samples was analyzed by compression tests. Stress–strain curves were measured in a universal testing machine (Instron model 5500R6025). Experiments were performed at room temperature and at a strain rate of 10 s^{-1}. The maximum static strain was 75% for all the experiments.

Three mechanical properties were obtained from these experiments, elastic modulus, calculated as the slope of the initial zone of the stress–strain curves, density of absorbed energy, defined as the area under the stress–strain curve up to a 75% strain, and collapse stress, measured in the intersection between a parallel line to the stress–strain response at low strains and a parallel line to the plateau region of the stress–strain curve.

Results and discussion

Cellular structure

Cell size, cell density and anisotropy

Although the properties of a cellular material are mainly determined by its density, microstructure also plays an important role in the behaviour of a foam, so a careful analysis of foam cellular structure can be useful for the comprehension of its response.

In this study, as different foaming processes are being used, it is necessary to know how each of them affects to the microstructure. Therefore, in the case of CO_2 dissolution, it should be analyzed the effect of density, and in addition if the restricted growth could affect in somehow the cellular structure of so-produced materials. On the other hand, in the case of samples made using azodicarbonamide, the effect of density as well as the influence of blowing agent content should be analyzed.

Figure 2 shows micrographs of PP foams produced using CO_2 as blowing agent. Several assertions can be pointed out from the observation of those micrographs.

First of all, as it can be observed, foams exhibit a completely closed cell cellular structure (this was confirmed afterwards with open cell content measurements). As it was mentioned in "Introduction", the base polymer used was a linear PP, therefore accomplishing closed celled foams indicates a proper control of foaming parameters (mainly foaming temperature and pressure drop).

On the other hand, it is easily inferred from the previous micrographs (Fig. 2) that as density decreases more anisotropic structures are obtained. The more dense samples (D1) exhibit an isotropic cellular structure, but as density of the samples decreases (expansion ratio increases) cells become oriented in the expansion direction (Fig. 1). In order to quantify this effect, the anisotropy ratio (R) of the samples was measured (Fig. 3a). While for D1 samples anisotropy ratio value is close to 1 (isotropic material) for D4 samples values around 2 are reached. Obtaining such anisotropic structures is connected with the restricted growth of the foam inside the mould. As diameter of the precursor is equal to the diameter of mould

Fig. 2 Micrographs showing the cellular structure of polypropylene foams produced using CO_2 as blowing agent
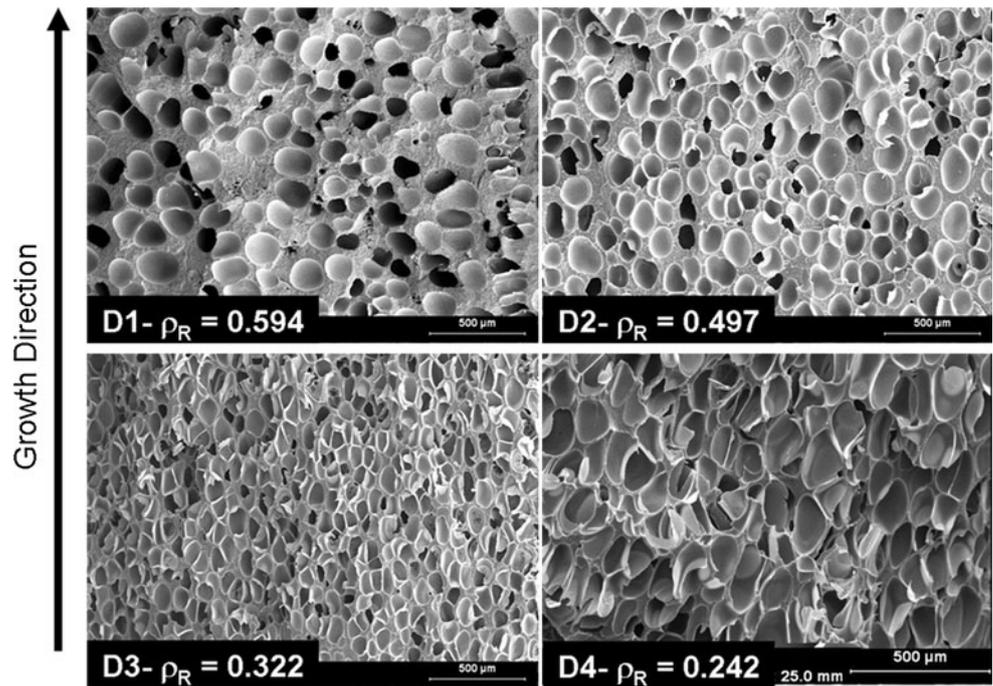
cavity, expansion of the sample may occur only in one direction.

Cell size as well as cell density of those foams were measured. Results are shown in Fig. 3b. It can be observed how cell size decreases as density does except for D4 samples where cell density increases as density does, once more except for D4 samples. So it seems that the lightest samples do not follow the same tendency as the others being the reason the foaming process itself.

The results obtained for D4 samples can be due to the combination of various effects. On one hand, for those samples, autoclave remains open after depressurization steps and the absence of a counter pressure could lead to larger cell sizes. On the other hand, a decrease in foaming temperature and an increase in the saturation pressure can lead to an increase in the amount of CO_2 dissolved in the polymer allowing cells to be able to grow large. Finally, D4 samples are the ones with the highest expansion ratio; as the cell expansion increases, cell wall thickness decreases, and the rate of gas diffusion between cell walls can increase leading to coalescence phenomena and thus decreasing cell density.

Figure 4 shows micrographs of PP foams with similar relative densities (around 0.5) blown using different amounts of azodicarbonamide. All of them exhibit an isotropic cellular structure being cell size smaller and cell density higher as azodicarbonamide content increases. This effect is achieved for all the analyzed density values, and can be evaluated in Fig. 5 where cell size (a) and cell density (b) are plotted as a function of azodicarbonamide content. Chemical
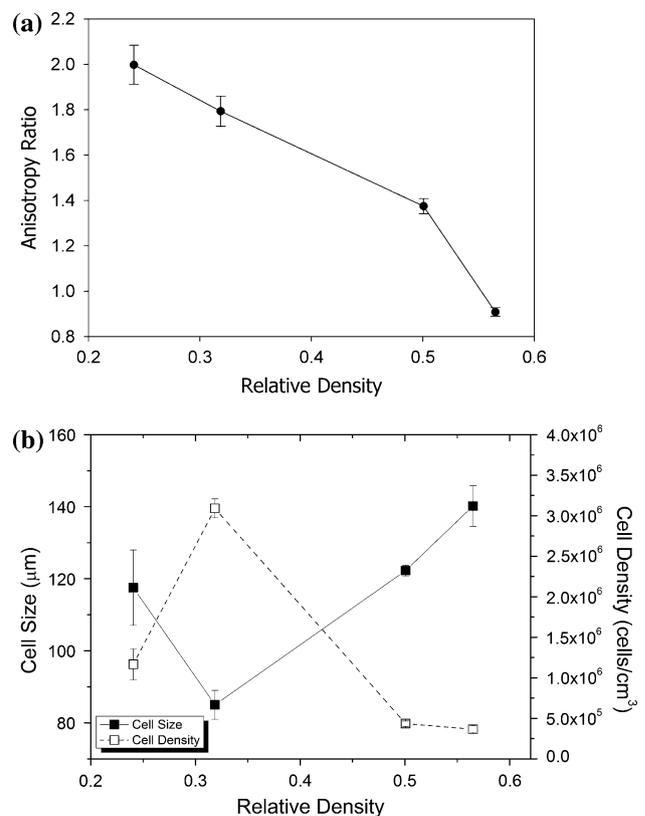
Fig. 3 a Variation of anisotropy ratio with relative density for polypropylene foamed by the modified pressure quench method. b Cell size and cell density of polypropylene foams produced using CO_2 as blowing agent

Fig. 4 Cellular structure of polypropylene foams with relative density 0.5 and produced using different amounts of azodicarbonamide
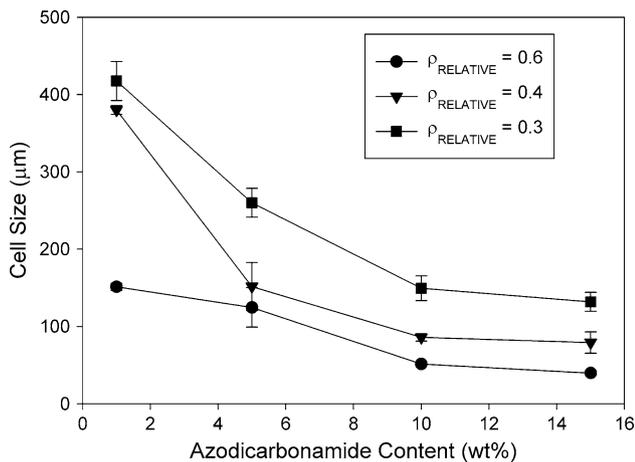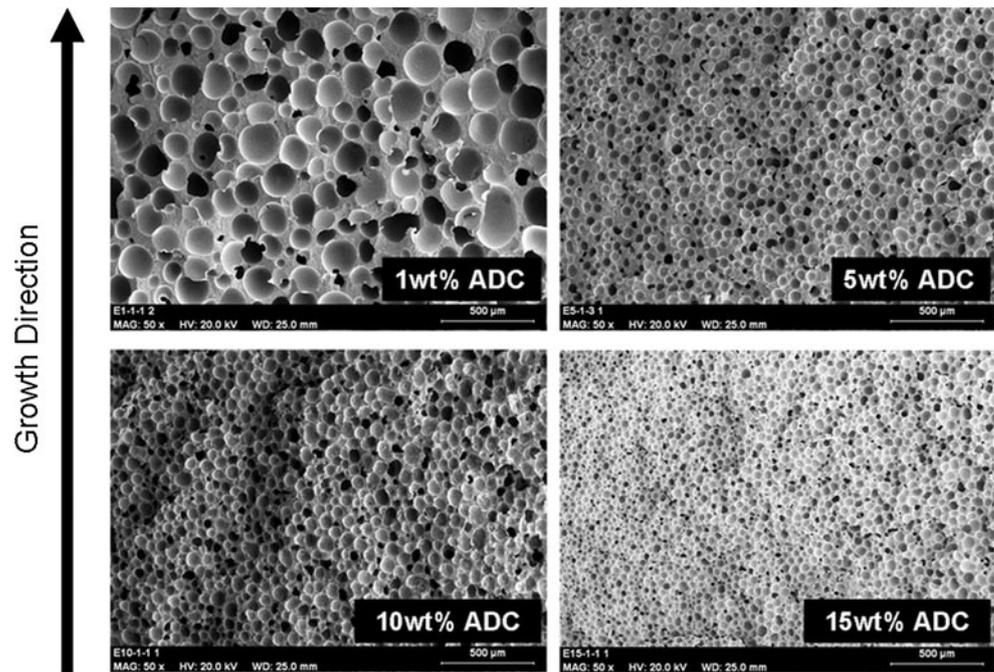
Fig. 5 Cell size of azodicarbonamide blown samples

blowing agents such as azodicarbonamide are known to be self-nucleating [2] so as blowing agent content increases a higher number or nucleating sites are available leading to higher nucleation rates and smaller cell sizes.

Comparing the results obtained using both types of processes (Figs. 3, 5), it can be concluded that the restricted growth only lead to anisotropic structures in the case of CO_2. Moreover, using chemical blowing agents, smaller cell sizes and higher cell densities are achieved.

Cell size distribution

It is known that large and non-uniform cells can have a negative influence on mechanical response [2, 3, 25]. Typically, histograms of the cell size distributions are plotted and afterwards compared. Due to the high amount of samples included in this study and in order to be able to easily compare the results obtained for both processes a standard deviation coefficient of the cell size distribution (SD), has been calculated according to Eq. 2 [26, 27]:

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

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 measures the width of the cell size distribution.

Results (Fig. 6) show clear differences between the samples produced using azodicarbonamide or CO_2. For relative densities higher than 0.4, smaller values of SD are achieved using azodicarbonamide while for relative densities smaller than 0.4, smaller values of SD are obtained for CO_2 blown samples. Moreover, as density decreases SD increases for samples made using ADC. On the contrary, for samples made using CO_2, SD decreases as density does.

There is also a clear influence of blowing agent amount. The smallest values of SD are obtained for high azodicarbonamide content (10 and 15 wt%) while when lower amounts of blowing agent are used, SD values are between two and three times higher.

Open cell content

It was found that open cell content for PP samples made using CO_2 was very close to 0%; on the contrary for samples produced using azodicarbonamide (Fig. 7) it was observed that this parameter increases as density is
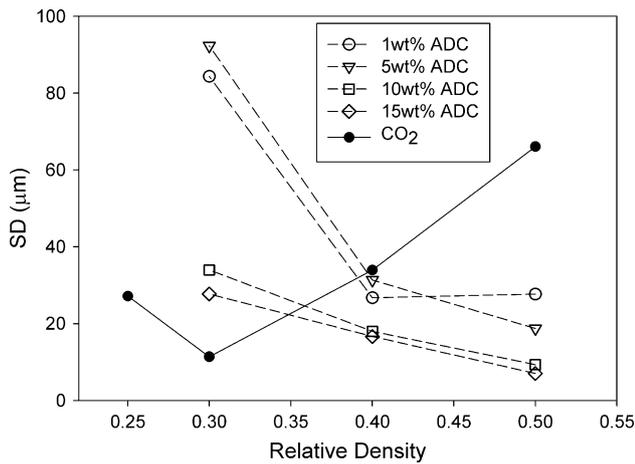
Fig. 6 SD coefficient for the whole collection of polypropylene foams
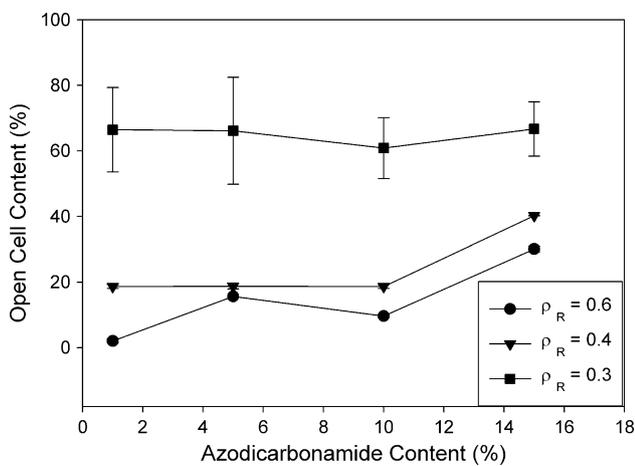
Fig. 7 Open cell content as a function of blowing agent amount for polypropylene foams with different relative densities

reduced. Regarding the influence of blowing agent amount, the higher values of open cell content are reached when the highest percentage of azodicarbonamide (15 wt%) is used. When such high amounts of ADC are used (15 wt%), the pressure generated inside the mould is much higher than for lower ADC contents. Due to this, the pressure drop during foaming is higher, and could lead to a significant opening of cell walls.

In addition, higher open cell contents are reached in the lightest samples ($\rho_R = 0.3$). As expansion ratio increases, the polymer is subjected to stronger elongational forces, hence, cell walls are thinner and consequently easily breakable.

Mechanical response

Using any of the two foaming processes it is possible to obtain perfectly moulded foams, so their mechanical properties could be determined by performing compression tests. Moreover, solid precursors from which each foam was produced were also analyzed. In the case of gas dissolution it was pure PP and for the improved compression moulding process, PP with the corresponding azodicarbonamide content.

Elastic modulus (E), collapse stress (σ_c) and density of absorbed energy (W) were determined for both precursors and foams from the stress–strain curves. Results corresponding to foams produced using CO_2 are summarized in Table 4. As it was expected, E, σ_c and W decrease when the density is reduced.

Experimental results corresponding to samples made using different percentages of ADC are presented in Table 5. In order to better understand the relationship between mechanical properties, density and blowing agent amount, experimental results for E, σ_c and W for foams, precursors and pure PP have been plotted as a function of ADC concentration (Fig. 8).

Comparing the results obtained for neat solid PP and precursors of PP with different percentages of ADC it is possible to detect that increasing the amount of blowing agent improves the stiffness (Fig. 8a). As it is marked in Fig. 8, PP with 15 wt% of ADC has an elastic modulus a 40.7% higher than pure PP.

On the other hand, there is a decrease in elastic modulus due to density reduction; this reduction varies from 52 to 84% in the analyzed interval of relative density. In addition, there is a slight decrease in E with the increase of ADC concentration. Samples made using 15 wt% of azodicarbonamide exhibit a poorer stiffness than samples produced using lower amounts of blowing agent.

Figure 8b shows the results corresponding to collapse stress. While solid PP becomes stiffer as ADC is added to the polymeric matrix, the addition of the chemical blowing agent has a negative effect in samples strength. By adding only 1 wt% of ADC to the PP matrix, collapse stress is reduced by around a 25%. This result indicates a loss of elasticity of the polymeric matrix with the addition of small amounts of azodicarbonamide.

Table 4 Results of compression tests for PP foams produced using CO_2 as blowing agent

Sample	E (MPa)	σ_c (MPa)	W (MJ/m^3)
Pure PP	582.44	34.27	44.20
D-1	208.19	9.87	20.35
D-2	138.51	7.04	15.10
D-3	99.90	3.08	5.20
D-4	68.82	1.48	2.70

All the values correspond to averages of three experiments performed in the same conditions

Table 5 Results of compression tests for PP foams produced using azodicarbonamide as blowing agent

Sample	E (MPa)	σ_c (MPa)	En_{ABS} (MJ/m^3)
Azodicarbonamide 15 wt%			
PP-15	983.10	28.16	38.86
A15-1	263.55	6.25	9.15
A15-2	110.26	2.38	5.52
A15-3	86.34	1.72	2.89
Azodicarbonamide 10 wt%			
PP-10	926.98	27.95	39.96
A10-1	178.97	5.70	10.11
A10-2	139.88	3.62	6.40
A10-3	97.79	2.45	3.36
Azodicarbonamide 5 wt%			
PP-5	795.74	28.62	40.35
A5-1	141.82	5.82	10.40
A5-2	197.90	5.17	8.12
A5-3	97.83	1.87	3.59
Azodicarbonamide 1 wt%			
PP-1	644.08	25.95	38.06
A1-1	279.49	8.05	13.02
A1-2	224.16	4.88	9.32
A1-3	93.24	1.96	3.65

All the values correspond to averages of three experiments performed under the same conditions

On the other hand, there is a significant decrease of collapse stress for foamed samples due to density reduction (between 76 and 94.4% for the analyzed density range). In this case, there is no significant variations with the changes in blowing agent amount although slightly higher values are obtained for samples produced using a 1 wt% of ADC.

Finally, Fig. 8c presents the results corresponding to the absorbed energy per unit volume (W). The results follow a similar trend to that observed for collapse stress. Once more, it seems that the addition of small amounts of ADC lead to a loss of elasticity of the PP matrix. In this case, foams produced using the smallest amount of ADC exhibit the highest values of W.

The results presented in Fig. 8a–c indicate that there are cross-effects of density, blowing agent amount and cellular structure affecting the mechanical performance.

With regard to the differences between materials from both processes, it can be observed (Tables 4, 5) that for similar relative densities, samples with 1 wt% of chemical blowing agent are stiffer than the foams produced using CO_2. However, samples made using CO_2 present a better mechanical performance in terms of strength (collapse stress) and energy absorption capacity. The presence of residues coming from ADC decomposition in cell walls of PP foams produced by the improved compression moulding
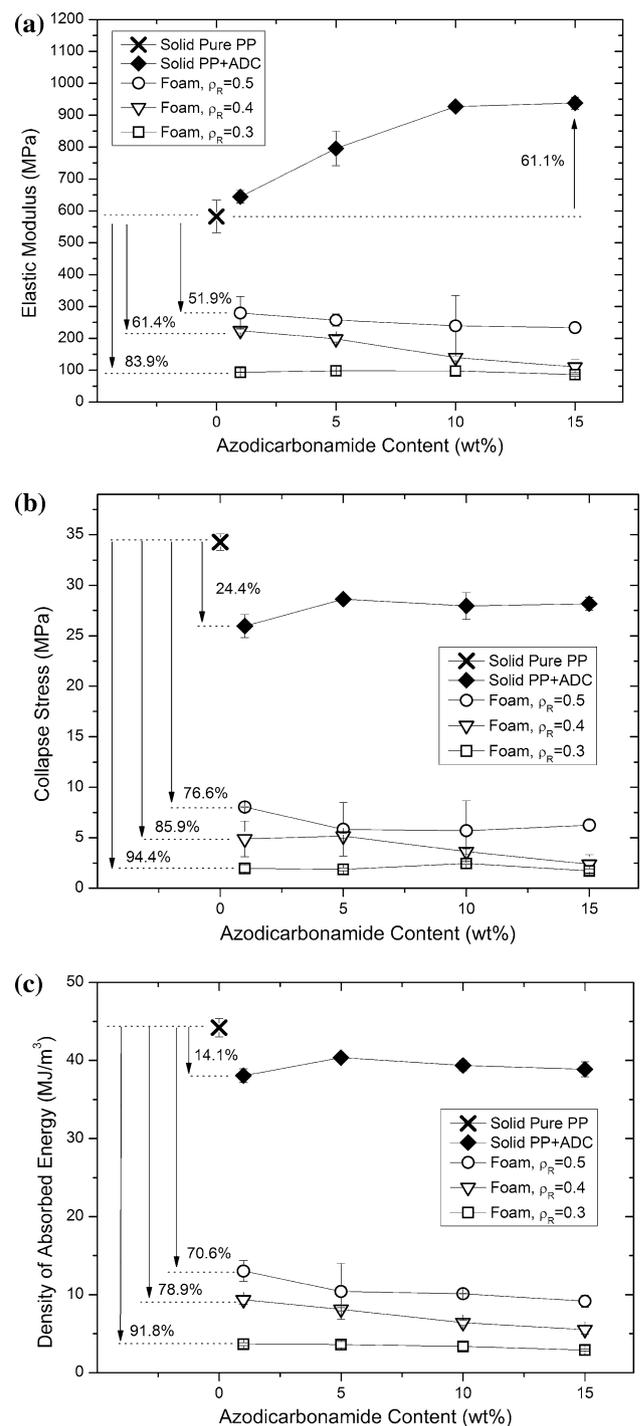
Fig. 8 Mechanical properties of PP foams with different densities produced by the improved compression moulding using different ADC contents. **a** Elastic modulus, **b** collapse stress, **c** density of absorbed energy

route, lead to a detriment of polymer elasticity and hence to a poorer mechanical response above the elastic limit.

In order to analyze if cell size is affecting the mechanical response, elastic modulus of PP foams produced using both foaming routes has been plotted as a function of
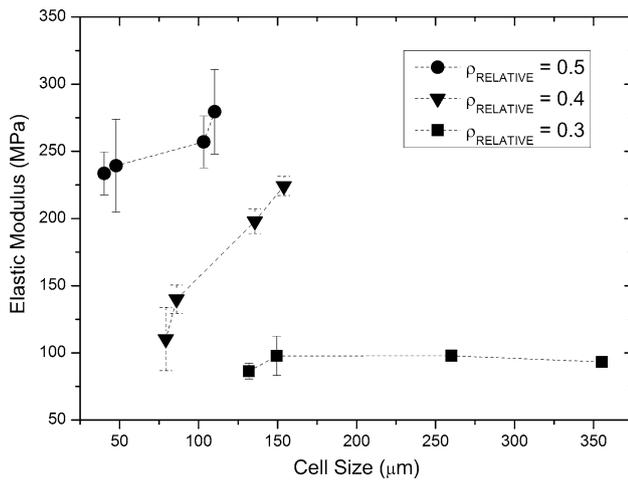
Fig. 9 Elastic modulus as a function of cell size for foams produced using the chemical blowing agent

Fig. 10 Relative elastic modulus of polypropylene foams versus relative density

average cell diameter (Fig. 9). There is a significant decrease in elastic modulus as cell size decreases for ADC-blown foams at relative densities equal or higher than 0.4. On the other hand, for relative densities lower than 0.3, elastic modulus is almost constant. As it was previously mentioned, smallest cell sizes are obtained when high ADC concentrations are used; at the same time, this high concentrations lead to higher open cell contents and hence to a decrease in mechanical performance. At low relative densities, although cell size decreases as ADC content increases, open cell remains constant (Fig. 7) thus leading to a similar mechanical response of the foams.

To better understand the effect of cellular structure on the mechanical response of the whole collection of studied foams, experimental data have been also analyzed in terms of relative properties, i.e. the property of the foam divided by the property of a reference solid. The solid from which each type of foams were produced (pure PP for CO_2 blown samples and PP with ADC for azodicarbonamide blown samples) has been used as reference material.

The analysis of mechanical properties in terms of relative values, apart of clarifying results can provide information about the effect of cellular structure on the mechanical response of produced PP foams.

In addition, experimental data have been compared with theoretical estimations obtained using a potential law of relative elastic modulus versus relative density (Eq. 3) with exponent $n = 1$ and exponent $n = 2$. C was assumed to be 1 in these estimations [21, 22, 25]

$$\frac{E_F}{E_S} = C\left(\frac{\rho_F}{\rho_S}\right)^n \tag{3}$$

where E_F and ρ_F are the foam elastic modulus and density and E_S and ρ_S are the modulus and density of the reference material used in each case.
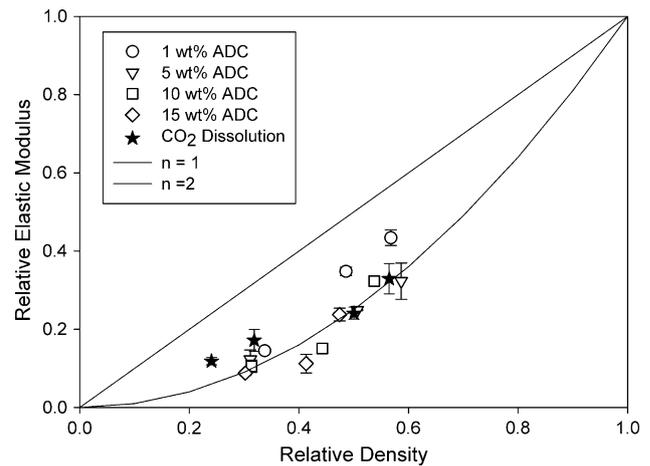
Values of n between 1 and 2 are typical for a wide amount of cellular materials [25], therefore it is expected that most foams, including the analyzed ones would have properties between these two limits.

Relative elastic modulus of the analyzed foams as a function of relative density is shown in Fig. 10. As it can be observed, both gas dissolution foams and azodicarbonamide blown foams exhibit values of n between 1 and 2. Moreover, it can be inferred that mechanical properties clearly depend on the foaming technique used to produce them.

At relative densities higher than 0.4 the stiffer materials are the foams made using the lowest amount (1 wt%) of azodicarbonamide while at relative densities lower than 0.4 the stiffer materials are the ones produced by CO_2 dissolution. Samples made using the smallest amount of azodicarbonamide are the ones with the smaller open cell content (see Fig. 6). Thus, although samples containing higher azodicarbonamide amounts (10 and 15 wt%) present smaller cell sizes, they exhibit a poorer stiffness.

It was previously said that samples produced using the physical blowing agent exhibit a closed cell structure so, although samples made using 1 wt% of azodicarbonamide present a higher open cell content, their mechanical response is much better.

The explanation of this behaviour lies in the differences found in cell sizes distribution (see Fig. 6). It was concluded after analyzing sample's microstructure that at relative densities higher than 0.4, the samples produced using a chemical blowing agent exhibited a more uniform cell sizes distribution (this is smaller values of SD).

It is known that a lower dispersion in cell sizes enhances mechanical behaviour of cellular materials [25, 26], and in this case, this narrower cell size distribution has a greater effect on stiffness than open cell content.

On the other hand at relative densities lower than 0.4, the behaviour of produced PP foams is the opposite, being the stiffer materials the ones produced by the gas dissolution technique. The results seem to be due to several reasons: an almost zero open cell content, a very uniform cell sizes distribution (for $\rho_R < 0.4$ they exhibit the smallest values of SD, Fig. 6), and the presence of a highly oriented cellular structure induced by foaming inside a mould.

According to Gibson and Ashby [25] Eq. 3 becomes the following one (4) when it is considered the elastic modulus measured in the direction where cells are oriented:

$$\frac{E_{f-Z}}{E_S} = C\left(\frac{\rho_f}{\rho_S}\right)^n \cdot R \tag{4}$$

where E_{f-Z} is the elastic modulus measured in the direction in which the cells are oriented, E_S is the modulus of the solid polymeric matrix, ρ_f and ρ_S are, respectively, foam and solid density and R is the anisotropy ratio.

Therefore, at equal relative density, an anisotropic foam ($R > 1$) will exhibit higher specific properties than an isotropic one ($R = 1$).

Collapse stress values obtained from compression tests have been also analyzed in relative terms and are shown in Fig. 11. Moreover, experimental data have been fitted to a power law equation (Eq. 5):

$$\frac{\sigma_F}{\sigma_S} = C\left(\frac{\rho_F}{\rho_S}\right)^n \tag{5}$$

where σ_F is collapse stress value of the foam, σ_S is collapse stress of solid material (each precursor in this case) and $\frac{\rho_F}{\rho_S}$ is the relative density of the foams [22, 25].

Values for n obtained from the fitting of experimental data are also given in Fig. 11. Values of n close to 2 are in agreement with predictions for an elastic collapse of the cellular structure [22]. In this study, the closest values to $n = 2$ are obtained for samples produced using the gas

Fig. 11 Relative collapse stress of PP foams versus relative density

dissolution technique ($n = 2.24$) and the ones produced using 1 wt% of chemical blowing agent ($n = 2.17$) and those produced using 15 wt% of chemical blowing agent ($n = 2.3$).

Gibson and Ashby [25] define the Young's modulus anisotropy ratio as the ratio between the modulus measured in the direction of maximum orientation of pores (E_L) and the modulus measured in the transversal direction (E_T). This parameter is a function of anisotropy ratio (R) and is defined as:

$$\frac{E_L}{E_T} = \frac{2R^2}{1 + (1/R)^3} + (1 - \phi)\frac{2R}{1 + (1/R)} \tag{6}$$

where R is the anisotropy ratio, E_L and E_T are the elastic modulus in the longitudinal direction (LD) and the transverse direction (TD), respectively. ϕ is the fraction of solid in the cell edges.

Performing a similar analysis for plastic collapse stress they find the following equation:

$$\frac{\sigma_L}{\sigma_T} = \frac{2R}{1 + 1/R} \tag{7}$$

where σ_L and σ_T are collapse stress measured in longitudinal and transversal direction and R the anisotropy ratio.

Therefore, the modulus depends strongly on anisotropy than strength; cells with an R value of 2 have a modulus anisotropy of nearly 8 and a strength anisotropy of around 2.6. On the other hand, Eq. 7 indicates that cells are stronger in the orientation direction, even though the anisotropy in strength is not as large as that in stiffness (Eq. 6).

Hence, in our case, we can observe a great effect of anisotropy in the elastic modulus but not in the collapse stress for CO_2 blown samples. The good behaviour of these samples in terms of strength should be due to their more elastic cell walls (there is no residues from blowing agent) and to their zero open cell content.

On the other hand, samples made using 1 and 15 wt% of ADC have a mechanical performance similar to CO_2 blown samples. Samples with 1 wt% have a very small amount of ADC residues in cell walls (so elasticity of cell walls should be similar to that of neat polymer), and they combine a small open cell content with a fine cell size. PP foams made using 15 wt% of azodicarbonamide have the highest open cell content and a huge amount of residues of ADC in their cell walls but they have the most uniform cell size distribution (see Fig. 6) which seems to compensate the previous effects giving a reasonable strength.

These results seem to indicate that cell size distribution plays a key role in the mechanical response in terms of strength of PP foams.

Finally, Fig. 12 shows values of relative density of absorbed energy as a function of relative density. In this
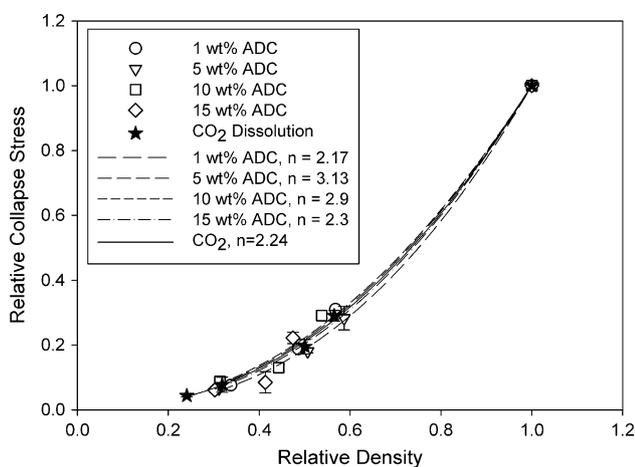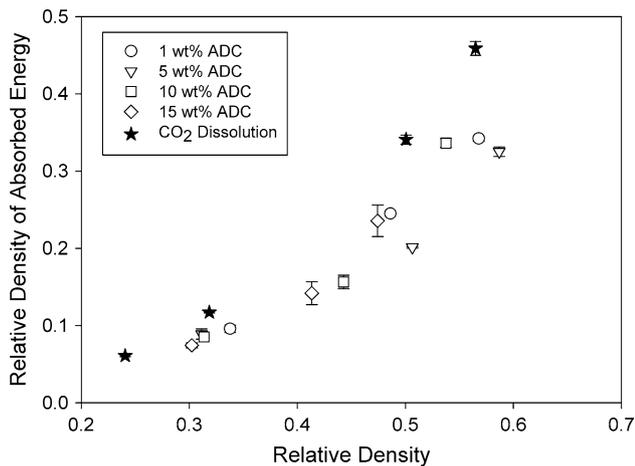
Fig. 12 Relative density of absorbed energy of polypropylene foams versus relative density

case, it can be clearly inferred from the figure that the materials produced by gas dissolution have the higher absorption capacity along the whole range of analyzed densities. Between materials made using ADC, the better performance in terms of energy absorption is obtained for samples containing 1 wt% of chemical blowing agent.

So, in this case it seems that the key parameter is a high elasticity and a zero open cell content. Foams made by the improved compression moulding route present open cells as well as residues of the chemical blowing agent in their cell walls which became them less elastic and hence they exhibit a poorer energy absorption capacity.

Conclusions

Moulded PP foams with relative densities between 0.25 and 0.6 have been successfully manufactured using two different foaming processes, gas dissolution and improved compression moulding. It has been proved that by means of both processes final density of the foams can be controlled. The accuracy of experimental density values compared with nominal ones demonstrates a proper control of the foaming parameters involved in both processes. Moreover, it should be mentioned that one of the goals of this work was obtaining moulded foams by the gas dissolution technique. Up to now, and as far as we know no papers reported such accurate control of final density and shape of CO_2 blown PPs.

It has been proved that depending on the chosen foaming process, blowing agent type and blowing agent amount a wide variety of cellular structures can be obtained. Combining the restricted growth in a mould and the pressure quench method highly anisotropic structures can be achieved. It was also observed that this combination leads

to completely closed celled PP foams which could be considered a significant achievement taking into account that a linear conventional PP grade was used for the study (instead a highly branched one).

By using different amounts of chemical blowing agents, foams with different open cell content and diverse cell sizes can be manufactured.

Mechanical response of the samples has been analyzed, concluding that mechanical properties of the materials strongly depend on the method and formulation used to produce the foams. Stiffness at high relative densities can be improved using the improved compression moulding technique due to the more uniform cell size distribution obtained for 1 wt% ADC samples, however, at low relative densities the optimum cellular structure to maximize stiffness is the one obtained by the gas dissolution technique due to their high anisotropy ratio and zero open cell content. The differences obtained in strength are small. In terms of strength, the best materials are the ones made by the gas dissolution followed by the ones made using the lowest azodicarbonamide content. In addition samples produced using CO_2 have a better performance in terms of energy absorption. Those last results can be explained considering the loss of elasticity of PP matrix due to the presence of residues coming from ADC decomposition in the samples produced using chemical blowing agents.

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