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Morphological Analysis of Polyethylene Foams with Post-use Material Incorporated

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Summary

This study investigated the morphology of low-density polyethylene (LDPE) foams with post-use polyethylene (p-PE) incorporated. Samples manufactured using compression molding were analyzed through scanning electron microscopy. Micrographs were treated using the software Image Tool for Windows, version 3.00. This allowed the determination of cell size (0 – 2500 μm) and cell area (0 – 1500 .10^3 μm^2) distributions. The research found that all compositions with p-PE material incorporated (15, 30, 40, 50 and 70% w/w) had similar morphologies, except the composition with 70% of p-PE, which gave a more significant increase in the amount of smaller cells. In comparison to samples with virgin LDPE only, all samples with p-PE showed an increase in cells with smaller areas (< 60μm) and smaller diameters (< 850μm^2), especially those with 70% p-PE. This finding may be explained by the smaller melt flow index of the p-PE (0.60 $g.min^{-1}$) in relation to LDPE (l.74 $g.min^{-1}$), which hinders cell growth. The addition up to 70%, of p-PE in formulations which contain 5% of azodicarbonamide leads to PE foams with ideal density ranges for use as packaging (30 to 70 $kg.m^3$).

Introduction

The United States, European countries and Japan have used plastic foams since 1960. However, only from the 1980's onwards did consumption increase with the development of new markets, technologies and applications, such as packaging used as protection against impact and vibration of fragile products. The shoes, civil construction, and automotive industries are also potential markets [1].

Almanza et al., [2] analyzed the microstructures of commercial polyethylene (PE) foams of different densities where N_2 was used as the blowing agent. They found that these foams have present an isotropic cellular structure and a lack of blowing vestiges on the cells' walls, and that the cell shapes were very similar for foams of different densities.

Zhang et al., researched the density and other the morphological aspects of high-density polyethylene (HDPE) foams, using HDPEs with different molecular weights. The author used scanning electron microscopy (SEM) micrographs and the image

analysis program Image-Pro Plus to evaluate the cellular structure, and to measure the average diameter of the cells (D), through the equation $D = d/(\pi/4)$, where d is the average diameter measured on the micrograph. This equation is found in the appendix of the norm ASTM D 3576. Increasing molecular weight of the HDPE, which may be correlated to increasing viscosity, generates smaller cells. A higher PE viscosity leads to a stronger resistance to blowing [3].

Zhang et al., also measured the elastic modulus, and HDPE foams' tension and flexion properties, comparing the data obtained with several proposed models to predict cellular material properties, in order to verify which model best fitted the obtained results. Increasing HDPE molecular weight changes the behavior of the material tension properties from fragile and brittle to ductile [4-6].

Zhang [7] studied the morphology of low-density polyethylene (LDPE) foams and also HDPE foams with azodicarbonamide as the blowing agent. For LDPE foams cell size increases with the amount of blowing agent used. The same behavior has been for the HDPE, although in lower intensities. This can be attributed to the fact that HDPE has a linear structure, while LDPE has a highly-branched structure that allows a better blowing agent diffusion through the chains. Since the blowing agent azodicarbonamide has a decomposition temperature higher than the PE processing temperature, zinc oxide is used to reduce this parameter to working conditions between 170 and 180º C [8].

Gendron [9] studied the effect of using poly(ethylene-co-octene) with different melt flow indexes, as well as the effect of using different cross-linking agent amounts, on foam density and cell size. The use of a cross-linking agent is necessary to maintain the foaming process, and to prevent cell collapse. It is necessary to have a good balance between the resin viscosity and the amount of cross-linking agent used, in order to achieve optimum foam characteristics.

Zattera et al., [10] compared molecular, mechanical, morphological, thermal, and mechanical-dynamic properties of post-use PE, derived from urban waste, in relation to the virgin polymer. They reported that post-use PE has similar properties to virgin PE.

The cross-linking agents most used in the production of poly[(ethylene)-co-(vinyl acetate)] (EVA) expanded sheets are dicumyl peroxides and bisperoxide. Zattera et al., [11] analyzed the influence of the degree of cross-linking on the mechanical properties of mixtures of cross-linked post-use EVA (EVAc), which originates from the shoe industry, and an urban PE waste. The addition of dicumyl peroxide induced significant changes in mechanical properties due to the cross-linking of PE and EVAc chains; significant softening was observed for mixtures with dicumyl peroxide contents higher than 2 phr. It is proposed that the softening caused by dicumyl peroxide addition was related to a decrease in the degree of crystallinity [11].

Thermoplastic resin consumption in Brazil, in 2005, according to ABIPLAST (Brazilian Plastics Industry Association), was around of 4,213,000 tons, and PE is the most consumed thermoplastic, with a market share of 38% [12].

In a study carried out by LPOL/ISAM/UCS [13] in Bento Gonçalves, southern Brazil, in 2002, it was observed that for normal collections of urban waste, the amount of polymeric material is 14.6%, and the total PE and poly(ethylene terephthalate) (PET) corresponds to 78% of the collected polymers.

This study aimed to manufacture LDPE foams incorporating different proportions of post-use polyethylene (p-PE) and to investigate the effect of the use of different proportions of p-PE on foam morphology.

Experimental Methods

Materials and Equipments:

The LDPE used was type SX7012 from Petroquímica Triunfo S.A. (Triunfo – RS) and the p-PE was obtained from a local recycling company (Caxias do Sul – RS).
The formulation components were azodicarbonamide (Planagem CS4M Bayer S.A. – São Paulo - SP), dicumyl peroxide (Retilox Química Especial Ltda. – Santana do Parnaíba - SP), zinc oxide (Global Química Ltda. - São Paulo - SP) and stearic acid (Quimibrás Indústrias Químicas S.A. – Rio de Janeiro - RJ), used as blowing agent, cross-linking agent, activator, and process assistant, respectively.
For all the formulations, 50 g, were processed using a Banbury mixer (UCS/Eletron), a hot press (Paschal 100 ton) and a mold with 12 x 12 x 5 cm.

Preliminary Tests and Analysis:

Zattera [10] previously analyzed the types of PE present in p-PE using differential scanning calorimetry (DSC).
The melt flow index of LDPE SX7012 and p-PE was measured in a Dynisco Kayeness Polymer Test System, model D4001Hv, at temperature of 190°C and with a weight of 10kg (ASTM D1238).

Mixtures Tested:

The amount of blowing agent was fixed at 5% for all mixtures, with 0.5% cross-linking agent, 1.7% zinc oxide and 1.7% stearic acid by weight [8]. The proportions of LDPE and p-PE, used, are given in Table 1.

Table 1 – Proportions of LDPE SX7012 and p-PE (% weight) in mixtures

Amount of LDPE	Amount of p-PE
100	0
85	15
70	30
60	40
50	50
30	70

Preparation of Foams:

The components used to obtain the foams were processed in a Banbury mixer at 120°C for 10 minutes, with progressively increasing speeds from 2 to 10 rpm, aiming at the dispersion of formulation components. The pre-forms (non expanded material with a thickness of a few millimeters – around 3 and 5 mm) were placed in a mold and the foaming was carried out in a hot press at 190°C for 10 minutes with 5 t (322×10^5 $N.m^{-2}$). Molds were cooled in the press through cold-water flow. It was obtained expanded foam sheets of 5 centimeters thick (corresponding to the size of the mold itself).

Analysis and Testing of Foams:

The apparent densities of foams obtained were determined according to the standard ASTM D 3575.
The morphologies of foams were determined by scanning electron microscopy (SEM) using a Jeol JSM 6060 with 15x magnification (three samples for each composition). The SEM micrographs obtained were treated using the software Image Tool for Windows version 3.00 [14].

Results and Discussion

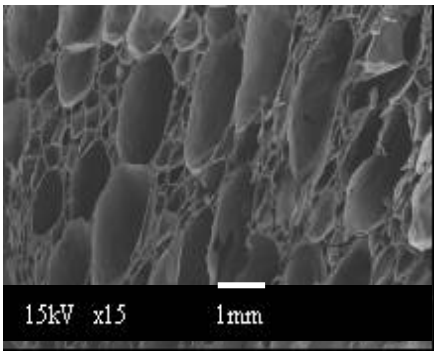
The characterization of the p-PE, by DSC, indicated that this material is a mixture of HDPE and LDPE, with two melt temperatures (110°C and 125°C).
The LDPE SX7012 and p-PE had melt flow indexes of 1.74 ± 0.16 $g.min^{-1}$ and 0.60 ± 0.01 $g.min^{-1}$, respectively.
The apparent densities of the foams obtained using compression molding are given in Table 2.

Table 2 – Apparent Density of LDPE/p-PE Foams (ASTM D3575)[15]

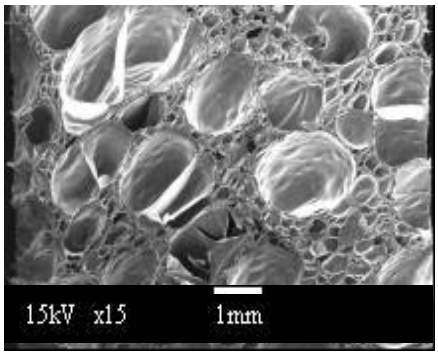
Proportion LDPE/p-PE (weight)	Apparent Density of Foam ($kg.m^{-3}$)*
100/0	61.47 ± 3.89
85/15	61.51 ± 1.99
70/30	62.21 ± 1.81
60/40	65.07 ± 3.09
50/50	64.40 ± 0.14
30/70	63.09 ± 0.38

* Although ASTM D3575 recommends the use of one sample for each foam formulation to measure density, in this study five samples were used, and the density given is the average value followed by the standard deviation.

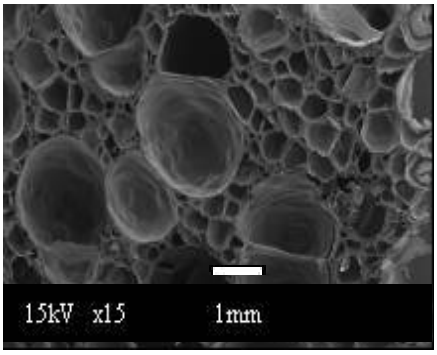
Mixtures comprised of over 70% p-PE were tested, but these samples gave the lowest foaming levels. Such high amounts of p-PE inhibit the complete filling of the mold and the formation of a uniform expanded material sheet, using 50 g formulations For the same reason, foams that use only p-PE were not manufactured.
Figure 1 shows the SEM micrographs for the different foam compositions tested. The analysis of images through the software Image Tool for Windows version 3.00 [14] allowed the determination of the cell size and cell area distributions for the different compositions tested. Without this software, an interpretation of data on foam morphology would not give reliable results. Differences in the foam cell characteristics of each composition cannot be measured or quantified simply by looking at the micrographs.



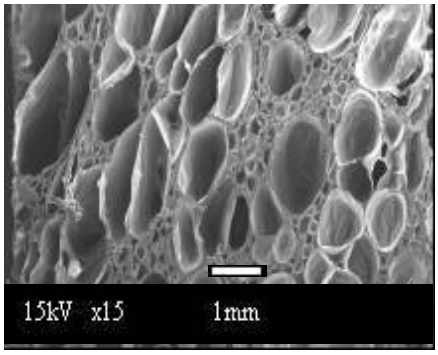
A



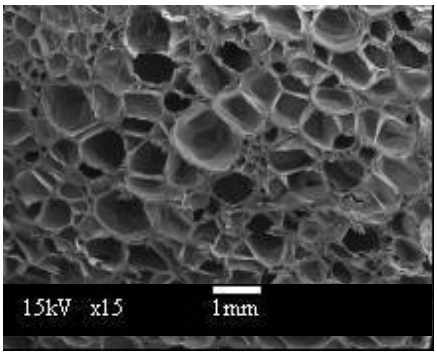
B



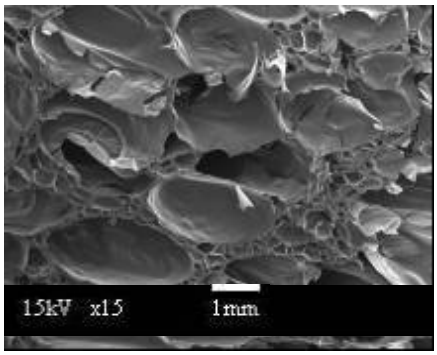
C



D



E



F

Figure 1 – SEM micrographs of PE foams (15x magnification) with LDPE/p-PE proportions (weight) of: 100/0 (A), 85/15 (B), 70/30 (C), 60/40(D), 50/50 (E) E 30/70 (F).

The results of the image analysis using the image software are shown in the graphs of frequency versus cell size distribuition (Figure 2) and frequency versus cell area distribution (Figure 3). The frequency is defined as the number of cells in a particular size range in relation to the total number of cells in that sample.

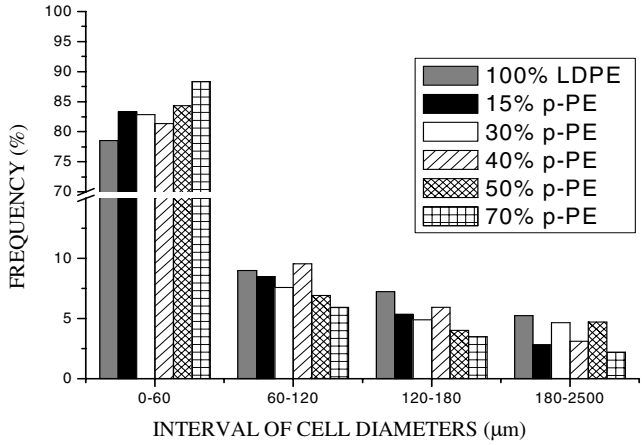


Figure 2 – Frequency x cells size range (μm) for each foams composition.

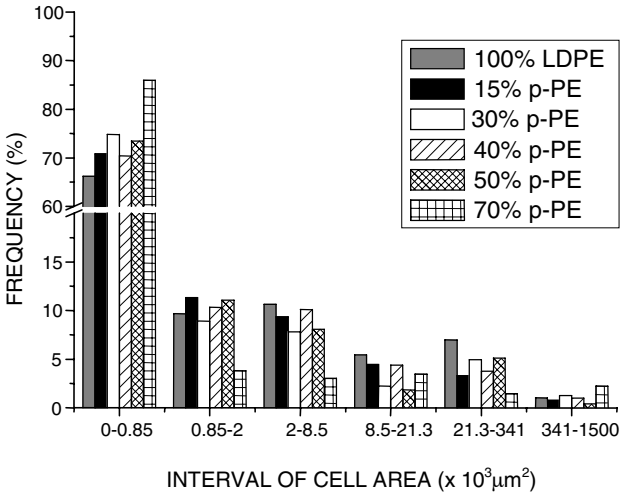


Figure 3 – Frequency x cells area range (μm^2) for each foams composition.

The compositions which included p-PE had a higher frequency of cells in the smallest size (0 to 60μm) and area (0 to 850μm^2) ranges than the composition with virgin LDPE only.
Cells with up to a 60μm diameter represented 78% of total cells for the foam manufactured with virgin LDPE, while for the foams obtained from LDPE/p-PE compositions of 85/15, 70/30, 60/40, 50/50 and 30/70 (by weight) these percentages were 83, 82, 81, 84 and 88%, respectively. The standard deviation to this interval of cell diameters (considering three samples for each composition) was smaller than 3%. In comparison to the foam obtained using virgin LDPE only, the samples with LDPE/p-PE 30/70 gave an increase of 12% in the frequency of cells in the range of 0-60 μm. The frequency of larger cell sizes generally decreased with increasing percentages of p-PE, with a 5% to 2% decrease in the frequency of cells in the range 180-2500μm when compared to the foam manufactured from virgin material in relation to the foam LDPE/p-PE 30/70, i.e. a reduction of 58% (Figure 2).
In relation to cell area, the cells with up to 850μm^2 represented 66% of total cells for the foam with virgin LDPE only, while for the foams obtained from LDPE/p-PE compositions of, 85/15, 70/30, 60/40, 50/50 and 30/70, these percentages were 71, 74, 70, 73 and 86%, respectively. In comparison to the foam obtained from virgin LDPE, the sample with LDPE/p-PE 30/70 gave a 30% increase in the frequency of cells in the area range of 0-850 μm^2 (Figure 3).
The increase in the amount of smaller cells with the increase in the amount of p-PE in the foam formulations is due the fact that p-PE has a lower melt flow index than LDPE SX7012 (0,60 g.min^{-1} and 1,74 g.min^{-1}, respectively). As the amount of p-PE in the formulation increases, the material viscosity increases and this hinders cell formation as observed for the formulation LDPE/p-PE 30/70.
The degree of foam anisotropy, defined by the ratio of larger to smaller cell sizes [7], is high because of the high amount of blowing agent used in the formulations. It was observed that the cells were elongated in the direction of the foaming material.
The results of this research for the relation between cell size and material viscosity, foams anisotropy, and cell form, are similar to findings reported by other researchers [3,7].

Conclusions

The compositions with the incorporation of p-PE gave an increase in the amount of cells with smaller sizes (0 to 60 μm) and smaller areas (0 to 850 μm^2) comparison to the composition with virgin LDPE only. The analysis of the morphology of LDPE foams with p-PE present in different amounts showed very similar cell size and cell area distribuition with up to 50% of p-PE. For foams with 70% of p-PE and above, there was a more significant increase in the frequency of cells with smaller sizes and areas. This may be explained by the lower melt flow index of p-PE in relation to LDPE. Results from this study are in agreement with studies carried out by other authors on the influence of molecular weight and material viscosity on foam morphology. The addition of up to 70% (weight) of p-PE in formulations that contain 5% of blowing agent leads to foams with ideal density ranges for use as packaging (30 to 70 kg.m^{-3}). Using LDPE/p-PE foams is viable for packaging applications for which an average density of 60 kg.m^{-3} is required, despite the high level of anisotropy of the foams due to the necessity for a high amount of blowing agent to be used in the formulations. In this study the amount of blowing agent was fixed at 5% (weight) for

all mixtures. Zhang et al. observed that there is a relationship between the amount of blowing agent and foaming ratio for contents until 2.5% (weight) [4-6].

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