



FOAM PROCESSABILITY OF TWO DIFFERENT HIGH MELT STRENGTH POLYPROPYLENE (HMS-PP).

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This work presents an experimental study on the foaming behavior of two high-melt-strength polypropylene (HMS-PP) with azodicarbonamide as a blow agent. One HMS-PP sample (sample B) presented melt strength of 49 cN and the other (sample C) 23 cN, values higher than the pure resins of 18 cN. The effects of increase azodicarbonamide concentration on the final foam characteristics have been thoroughly investigated by final morphology and toughness. The cell morphologies for the two HMS-PP were found to be significantly different. A slightly lower nuclei of cell was observed in the sample C than in the sample B. The experimental results indicated that sample B that present high value of melt strength had an important influence in determining this distinct morphology. The foam process used here did not reveal satisfactory, therefore the obtained material had not the desired density and showed high stiffness. However, modifications in the composition are being studied to can get a HMS-PP foam that presents low density without undertake the mechanical properties.

Introduction

The consumption of polypropylene (PP) in the foam market increased in the last years. This market is dominated by the amorphous polymers, such as polystyrene (PS), polyurethane (PU) and polyvinylchloride (PVC) about for over 50 years. Although, there are a number of other resins whose foams are developed in industries, for example: Polyethyleneterephthalate (PET), epoxy, silicone, fluoropolymer, polyisocyanurate foams¹, etc. The reason why PP foams are a relative latecomer to this market is related to the linear molecular structure of commercial PP. Therefore, PP has a poor melt stability required extensional property for the production of extruded low density foams with a fine controlled cell structure²⁻⁶.

The foaming of conventional linear PP in a continuous extrusion process is restricted by rheological properties especially their low melt strength. This characteristic, lead to a rupture of the cells walls under the elongational forces occurring during cell growth. So, the final foam has high amount of coalesced and open cells, which makes them unsuitable for many applications²⁻⁴. A way to improve the foaming behavior of polypropylenes is the incorporation of long chains branching technology using specific catalyst, irradiation or by reactive compounds creating the high melt strength polypropylene (HMS-PP), and rendered the extrusion of low density PP foams possible. The HMS-PP exhibits a pronounced strain hardening behavior if elongated in the molten state²⁻⁶.

Stange and Münsted⁴ in recent studies showed that using blends of PP with lower amount of long chain branching PP produced homogenous cellular structure and significant lower density. Another significant improvement of the foaming behavior of these samples was with respect to a higher expansion ratio, and a more homogenous cell size distribution reached with increasing content of the long chain branching.

As already mentioned to add chain branches onto PP backbone using gamma radiation is one of effective approaches to improve melt strength and extensibility of this material. Therefore, Ipen's polymer group together with Braskem (the leading Brazilian PP producer) with Embrarad (the leading Brazilian gamma irradiator) worked and evolved a national technology for the production of HMS-PP, using the combination of the knowledge of high energy radiation and different multifunctional monomer. Through this technology it's possible to produce HMS-PP with distinct values of melt strength. In this sense, in the present work two different HMS-PP were submitted to process to obtain foam processability. Two concentrations of Azodicarbonamide (AZDN) were used as blow agent for the nucleation of bubbles without using any nucleation agent. Finally, behavior of HMS-PP foams has been investigated by mechanical and density values. In addition, the effects of processing conditions on the final foam morphologies have also been examined through these experiments.

Experimental

Materials

The plastics materials used in this study were two high melt strength polypropylene obtained by Ipen/Embrarad technology. In this process the pure resin was submitted to the high-energy irradiation (gamma rays) in the presence of crosslinking agents. One HMS-PP sample (sample B) presented melt strength of 49 cN and the other (sample C) 23 cN, values higher than the pure resins of 18 cN. These values are higher than the original resin that was 18 cN. The melt flow index (230°C; 2.16 kg) is 1.8 for the sample B/HMSPP and 9.0 g/10 min for the sample C/HMSPP.

Experimental procedure

The HMS-PP resin were mechanically mixed with a proper proportion of paraffin oil, antioxidant agent (Irganox 1010) and two concentration (x quantity in the first case and the double concentration in the second case) of chemical blowing agent, Azodicarbonamide (AZDN). Then, the mixtures were fed into a twin screw extruder at a 40 min⁻¹ screw speed and temperature zone of 165; 175; 180; 185 and 195°C. After solidification of melt filament the prepared mixture was put into the mold of the foaming apparatus and heated up to a temperature of 230°C for 15 minutes, which is sufficiently long to achieve a homogenization of the dissolved gas in the polymer melt by diffusion. Azodicarbonamide decompose around 200°C. The foam samples were characterized by optical microscopy to evaluate the morphology. The samples were dipped in liquid nitrogen and then fractured to expose the cellular morphology.

The bars for the three point bending test had a cross section with 50 mm height, 8 mm width in the bending direction and 2 mm thickness perpendicular to it. Test samples were cooled to -60°C and heated under a strain-controlled sinusoidal tensile loading to 50°C at a heating rate of 2 °C/min. The maximum dynamic force used was 5N with amplitude of 60 µm. All measurements were performed over a wide temperature range at different frequencies of 1, 2 and 5 Hz.

Results and Discussion

The samples B and C presented a swelling when the mixture was extruder out of die, however the melt fracture phenomena increase due to adding excessive blow agent which was more evident for sample B₂. Obviously, the melt flow index of sample C foams is lower than that of samples B when the AZDN increase, as shown in table 1. This might be due to thermal oxidative degradation of the foams produced (extruder mixture), thermal degradation resulted in lower molecular weight.

Table 1- Results of melt flow index of the foam PP in comparison with the pure HMS-PP.

Samples	Melt flow rate (g/10 min)
B ₀ /HMSPP	1.80
B ₁	15.62
B ₂	32.12
C ₀ /HMSPP	9.00
C ₁	5.63
C ₂	12.26

In Figure 1 it's possible to observe the morphology of the samples foamed from sample B and C. As can be seen from Figure 1(a) a very inhomogeneous cellular structure with a broad variety of different cell sizes is visible. Especially in the bottom of micrograph, a high amount of unfoamed polymer matrix is found, although, it has many great bubbles in the center due to the coalescence and rupture of the cell wall creating open cell foams. When the concentration of blow agent increased, see Figure 1(b), a better distribution of open cells were observed. In this case the dispersion of the blow agent throughout the melt had been better than in the sample B₁ (Figure 1a).

Otherwise, the cell size in the sample C is smaller than sample B, Figure 1(c), and this sample presents high rigidity which decreases with the rise blow agent concentration, see Figure 1(d).

The melt of sample B proceeding from high HMS-PP (49 cN) has higher resistance to extensional deformation in the foam process; as a result sample B has the best foamability and shows a high elasticity unlike the rigidity of sample C, specially Figure 1(c).

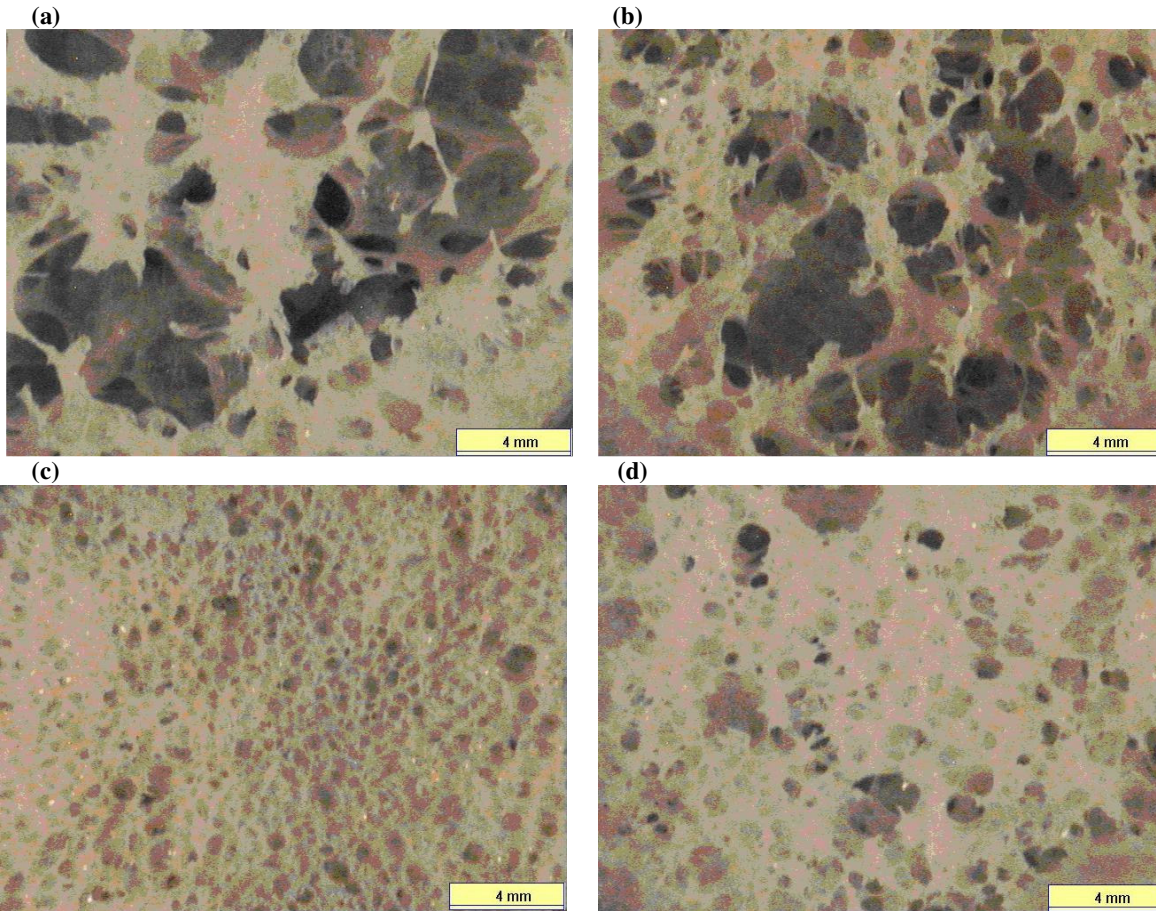


Figure 1 – Typical cell structure in HMS-PP foams: (a) sample B₁, (b) sample B₂, (c) sample C₁ and (d) sample C₂.

Park and Cheung⁵, shown that the coalescence of cells during foam processing is favored because the free energy level of the polymer/gas system will be lowered. Nevertheless cell coalescence occurs in foaming and consequently the cell-population density and mechanical properties are deteriorated. So, through this affirmation and from Figure 1 can be supposing that sample C probably have high elasticity modulus than sample B, even when the blow agent has been doubled. In Figure 2 this behavior can be visualized and proved for the sample C, however for sample B this behavior is contradictory, this trend can be explained through dispersion of AZDN by the polymeric matrix and by small size of cells.

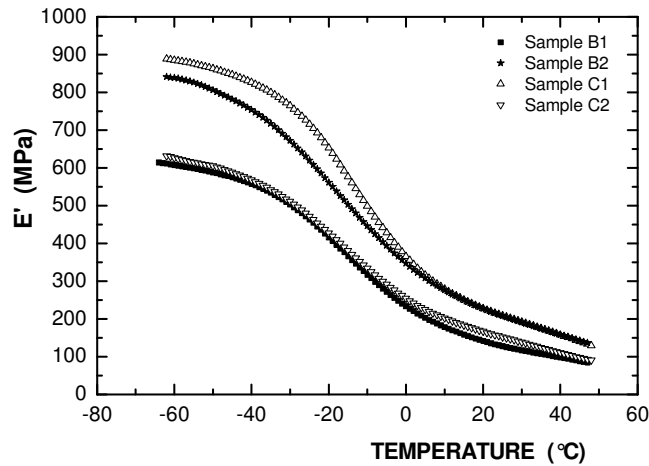


Figure 2- Modulus of elasticity as a function of temperature for all HMS-PP foams at frequency of 1 Hz.

The tensile results corroborate with the elasticity modulus for the samples as can be seen in the table 2. The enhanced tensile properties in the sample C more than sample B are due to rise quantity of polymeric matrix. After solidification foams samples C were clearly more stiffness in comparison with sample B proving again the results above mentioned. Finally, due to big bubbles being wasn't possible to obtain the density results by A method of ISO R1183.

Table 2 - Values of tensile strength and elongation at the break of the HMS-PP foams.

Sample	Tensile strength (MPa)	Elongation at the break (%)
B ₁	3.89 ±3.0	9.68 ±5.4
B ₂	2.97 ±1.8	17.67 ±7.8
C ₁	5.02 ±2.5	25.31 ±11.7
C ₂	4.71 ±3.1	26.71 ±9.3

Conclusion

Experimental studies were carried out to produce PP foams from two different high melt strength polypropylene using chemical blow agent. The experiments conducted in this study lead to the following conclusions:

- i-) The PP with higher value of melt strength, sample B, showed more appropriate to the expansion process with azodicarbonamide than sample C.
- ii-) High melt strength is beneficial to formation of a bigger amount of large cells. In the sample B most cells were opened and interconnected to each other more than in sample C.
- iii-) The cell-population increased as the amount of blowing agent increased for both samples.

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