FOAM PERFORMANCE OF A NEW HMS-PP

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Abstract

Foaming polymers is an important technological approach with economical and technical advantages in a range of applications, providing qualified products using less material and improving sustainability. Braskem has developed proprietary technology to produce High Melt Strength Polypropylene (HMS-PP), branded as the "AmPPleo" family, with long chain branching (LCB) suitable for foaming processes. The rheological properties have been evaluated in terms of viscosity, elasticity and melt strength, showing good foaming potential. Several large-scale foaming trials have confirmed laboratory results. These results showed stable process conditions, excellent foam properties, cell structure control using different chemical blowing agents and confident correlation of density versus gas amount using different gases (isobutene and CO_2). Foaming process parameters and final structures were very promising and demonstrated a very broad range of low densities (from 150 to 50 kg/m³), cell size control with different cell nucleation agents and the ability to maintain excellent foam characteristics with physical blowing agents.

Introduction

Long chain branch (LCB) insertion in polymer chains is the object of many fields of research, including catalyst systems, process development and post-reactor reactions[1,2,3,4,5,6,7,8].

Usually the first technological approach would be reactive extrusion to create branching in PP, but techniques involving free radical generation are usually limited to PP interaction with free radicals, where at temperatures higher than 120°C the β-scission is favorable instead of the branching process. A chemical suitable process might need to be developed.

Braskem developed a post-reactor chemical modification technology[9] where long chain branching is introduced. The objective of this paper is to discuss the AmPPleo properties and performance in different foaming conditions and compositions.

Materials and Methods

AmPPleo 1020GA HMS-PP produced by Braskem has a MFI of 2.0 g/10min (ASTM. D1238).

Reference linear material data used included a product with usual Molecular Weight distribution (catalyst 1) and one with broad molecular weight distribution (catalyst 2).

Samples were also analyzed in Rheotens 49.11, coupled in a Haake extruder at 190°C, with an acceleration of 60 mm/s^2 and a die distance of 60 mm in order to determine the Melt Strength following internal methodology.

The foaming processes were characterized in the Krauss-Maffei Berstoff GmBh (KMB) facility in Hannover, Germany, in a tandem system, 1st Extruder- ZE 40, Co-rotating twin screw extruder and a 2nd Extruder, KE 90 – Single Screw Extruder, coupled to an annular die, operating at 100 kg/h, using different gases (Butane and CO_2) as physical blowing agents. Densities were determined by internal KMB methods and it was confirmed by buoyancy gravimetric analyses according to ASTM 792.

Closed cell content was measured in a gas pycnometer Quantichrome Ultrafoam 1200e (V5.04.) following ASTM D6226.

Samples were foamed with special additivation as show in Table 1.

Table 1 – additives used in foaming process

Additive	Commercial name	Supplier
Talc	Finatalc M30	Mondo Minerals
CBA-1	Hydrocerol CF40E	Clariant
CBA-2	Ecocell 20P	PoliFil

Rheological Behavior

The first approach in characterizing HMS-PP is the measurement of the melt strength (MS) as a function of melt flow rate (MFR.)[10] In general, melt strength increases as molecular weight increases and melt flow decreases, as shown in Figure 1. The amount of melt strength increase with decreasing melt flow varies, depending on the specific processing used to produce the polymer. For example, different catalyst systems give different response to the melt flow as shown in

Figure 1. Some catalysts can provide melt strength as high as that of commercially available HMSPP grades at low melt flow. However, these linear materials are not viable options for processes requiring high elongational viscosity. It can be seen that changes in the catalyst system can result in some improvement in MS at levels similar to HMS-PP.

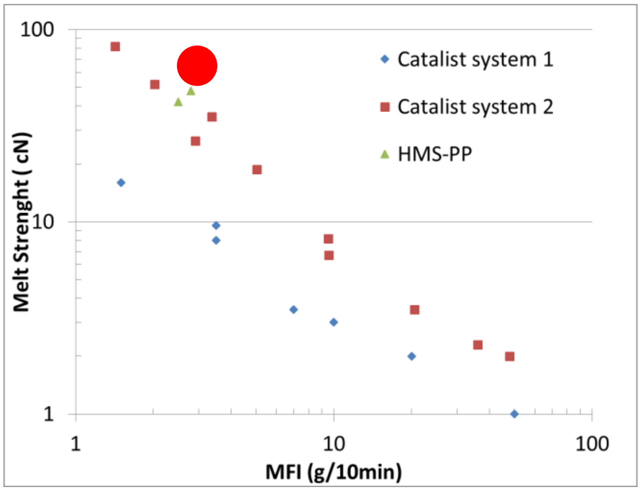


Figure 1 – MFI x Melt Strength for different Polymers.

However, MS data alone is not sufficient to evaluate HMS-PP performance. For processes such as foam, which require high elongational viscosity, melt elongation is also an important feature.

As reported in Figure 2, branched PP is differentiated from linear PP by the drawability at peak melt strength.

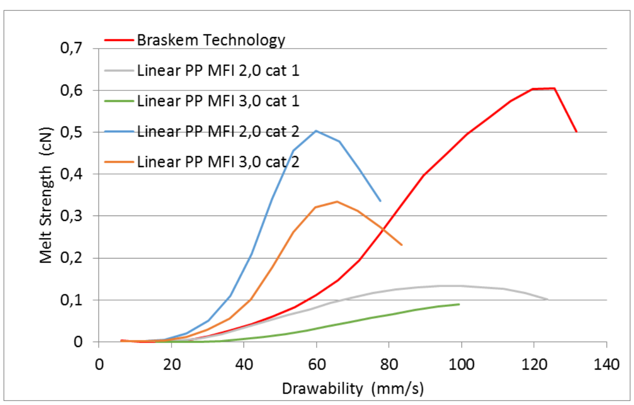
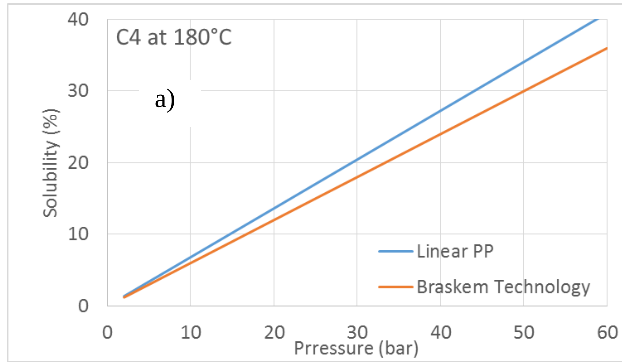


Figure 2 – Melt Strength profile for a HMS-PP compared to linear PP using different catalyst systems

Other rheological methods can also be used to characterize HMSPP. Both shear rheology and elongational viscosity measurements demonstrate the significant effects of branching on the melt behavior of HMSPP. These methods can be used to predict processing performance.

In addition to rheological properties, foam performance depends on crystallization control and gas solubility.[11,12,13]. Crystallization of Braskem AmPPleo 1020GA has been developed to provide a broad foaming window (crystallization control) and high gas solubility as shown in

Figure 3.



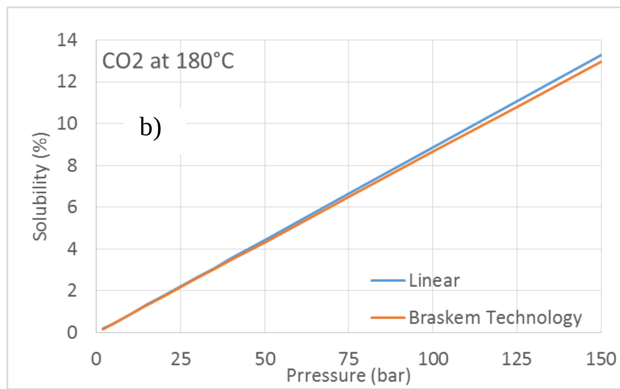


Figure 3 -AmPPleo 1020GA solubility in different gases a) Butane and b) CO_2.

Foaming Performance

Foam performance can be evaluated by measuring the response of density to gas feed content, process temperatures, and formulation including talc and chemical blowing agents.

Density x Gas amount

Figure 4 demonstrates that AmPPleo can achieve a wide range of densities, using several different physical blowing agents, specifically, CO2 and isobutene.

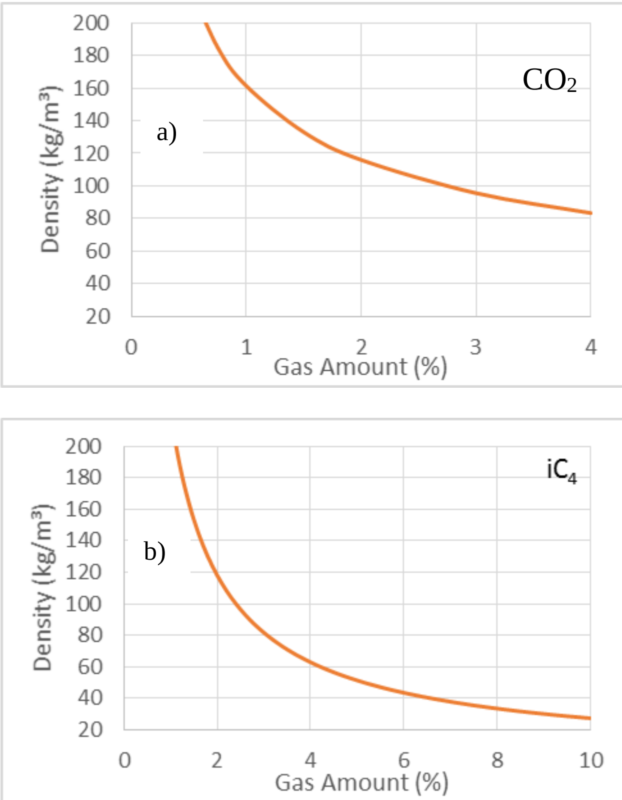


Figure 4 – Effect of gas feed amount on foam density for a) CO2 and b) Butane.

Optimum Foaming Temperature

Figure 5 confirms that the optimum foam temperature for AmPPleo HMSPP decreases with increasing gas feed concentration. The trend is expected, because higher gas feed leads to decreased melt viscosity. The optimum foam temperature also depends on the specific formulation, including the presence of nucleating agents.

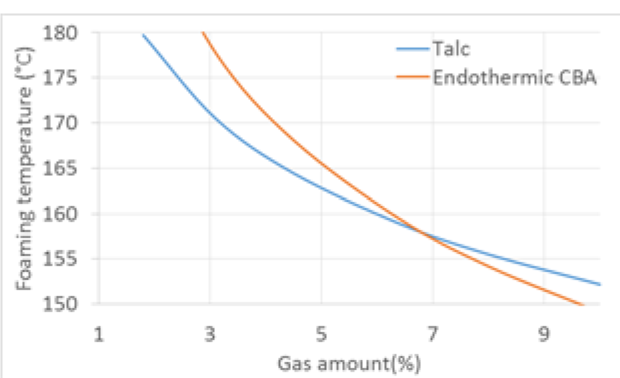


Figure 5 – Optimum foam temperature response to feed amount of C4 1.

Foam Characteristic with C4

Foam performance depends strongly on cell structure as well as density. Therefore, an HMSPP grade that is effective for low-density foam must offer the possibility of generating a high level of closed cells that support foam process performance or open cells for special applications.

Two key factors affect cell structure. The first is the cell count. The higher the cell count, the thinner the cell walls, which makes it much more difficult to maintain an intact structure. The second driver is the cell nucleation mechanism. For example, using talc as a cell nucleation agent presents another problem, because the talc can promote some defects in cell structure such being a source of open cells. The effect of talc concentration on AmPPleo cell count is show on in Figure 6.

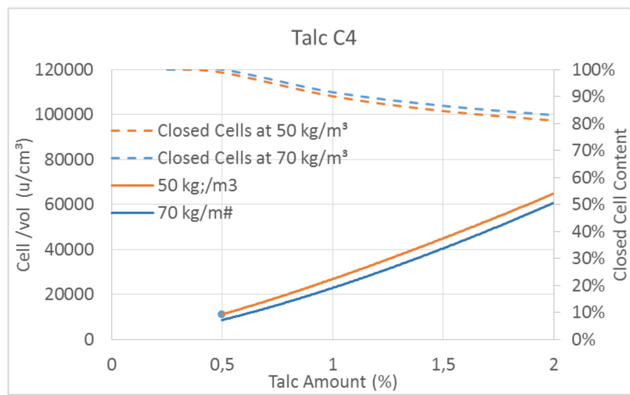


Figure 6 – Cell count and close cell content against Talc loading to C4 densities.

For both densities, there is a slow decrease in cell count, indicating that the talc effect on closed cell content is stronger than the decrease in cell wall thickness. It is an important conclusion which indicates how robust the AmPPleo may be for different final applications, mainly for large/medium cell sizes.

However, some applications require a more fine structure with a larger numbers of cells and also do not allow reduction in closed cell content. A solution is the use of CBA’s. These two CBA’s, 1 and 2, give different density responses using Butane, as shown in **Figure 7**.

Using different CBA´s the cell count increases at different rates. This is important for process control. It is one more important aspect in final product development.

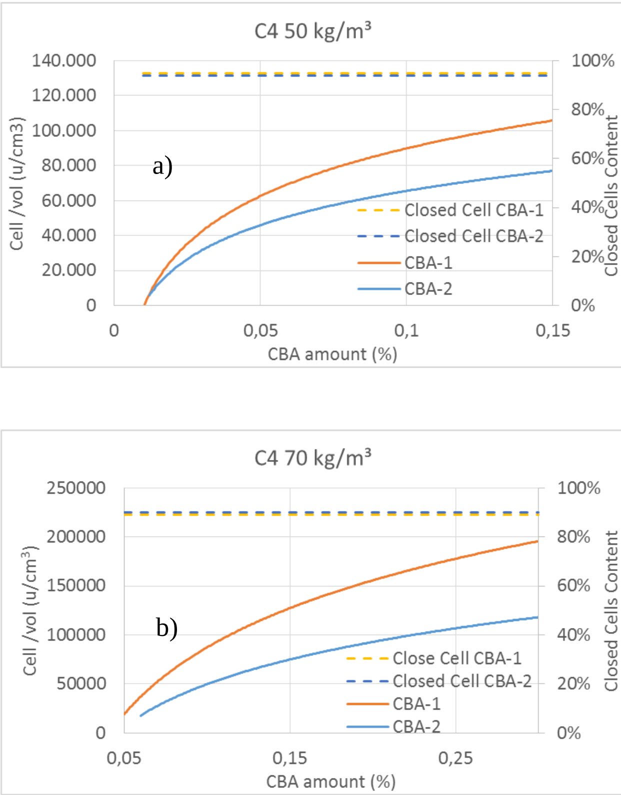


Figure 7 – Closed cell content and cell count using Butane and different CBA's at a) 70 kg/m³ and b) 50 kg/m³.

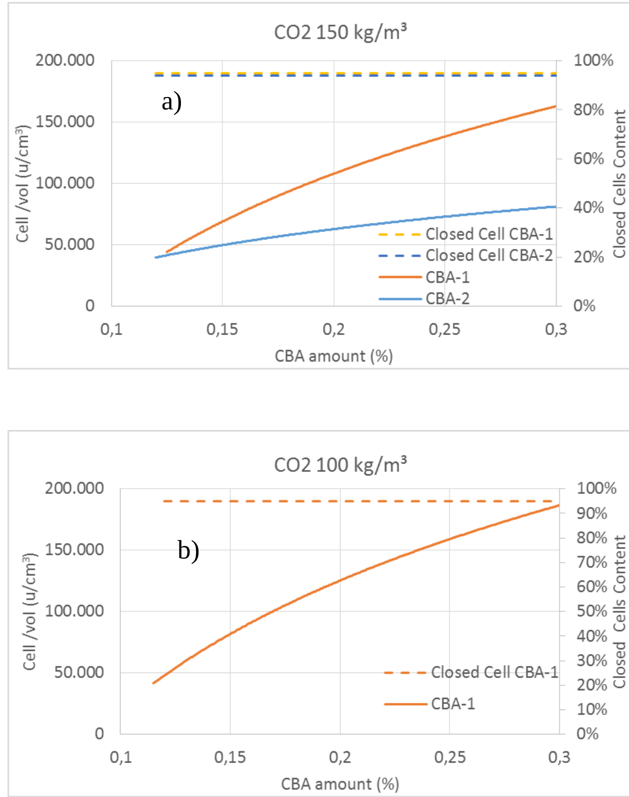


Figure 9 – Effects of CBA's on cell count and closed cells content using CO_2 as PBA: a) 150 kg/m³ and b) 100 kg/m³.

Foam Characteristic with CO2

The effects of density and cell nucleating agent on cell morphology are somewhat different for foams produced using CO_2 than for foams produced using butane. As shown in Figure 8, the cell count is more dependent on density, and less so on talc feed concentration.
Also, using CBA's increases the cell count to a greater extent than using talc; however, no changes in closed cells were observed.

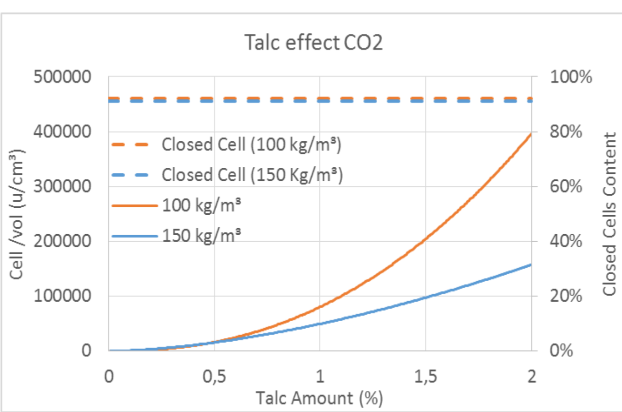


Figure 8 - Talc effect on cell count using CO_2 as PBA for different densities.

Conclusions

This paper demonstrates the melt rheological attributes and foam processing and performance properties of Braskem's new high melt strength PP, AmPPleo 1020GA. It also demonstrates the very good performance of the Braskem AmPPleo 1020GA in different foaming densities, compositions and structures. The broad processing window, with a suitable response to foaming temperature and nucleation create multiple density possibilities. AmPPleo is a new option in the market for PP foams development.

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