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Evaluation of Foaming Polypropylene Modified with Ramified Polymer

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Abstract

Polypropylene foams have great industrial interest because of balanced physical and mechanical properties, recyclability as well as low material cost. During the foaming process, the elongational forces applied to produce the expanded polymer are strong enough to rupture cell walls. As a result, final foam has a high amount of coalesced as well as opened cells which decreases mechanical and also physical properties. To increase melt strength and also avoid the coalescence effect, one of the current solution is blend PP with ramified polymers as well as branched polypropylene (LCBPP) or ethylene-octene copolymer (POE). In this research to provide extensional properties and achieve uniform cellular structures of expanded PP, 20 phr of LCBPP or POE was added into PP matrix. The blend of PP with ramified polymers was prepared by twin-screw extrusion. Injection molding process was used to produce PP foams using azodicarbonamide (ACA) as chemical blowing agent. The morphological results of the expanded PP displayed a non-uniform geometrical cell, apparent density of 0.48 g/cm³ and cell density of 13.9 $.10^4$ cell/cm³. Otherwise, the expanded PP blended with LCBPP or POE displayed a homogeneous cell structure and increased the amount of smaller cells (50–100 μm of size). The apparent density slightly increased with addition of LCBPP or POE, 0.64 and 0.57 g/cm³, respectively. Thus, the cell density reduced to 65% in PP/LCBPP 100/20 and 75% in the sample PP/POE 100/20 compared to expanded PP. The thermo-mechanical properties (DMTA) of PP showed specific stiffness of 159 $MPa.cm^{-3}.g^{-1}$, while the sample PP/LCBPP 100/20 increased the stiffness values of 10%. Otherwise, the expanded PP/POE 100/20 decreased the specific stiffness values at -30%, in relation to expanded PP. In summary, blending PP with ramified polymers showed increasing of the homogenous cellular structure as well as the amount of smaller cells in the expanded material.

Keywords: Polyolefin Foams, Azodicarbonamide, Ramified Polymers, Melt Strength.
PACS: 81.05.Lg

INTRODUCTION

Polypropylene foams have great industrial interest because of balanced physical and mechanical properties, recyclability, light weight as well as low material cost. However, foaming PP is not a simple task, mainly due low melt strength, which leads to cells walls rupture under elongational forces during cell growth [1]. As a result, the expanded grades of linear PP have a high amount of coalescence and open cells which decrease mechanical properties. To increase melt strength, one of the current solution is blend PP with branched polypropylene (LCBPP) as well as ethylene-octene copolymer (POE) [2, 3]. In this study to provide extensional properties and achieve uniform cellular structures of expanded linear PP, 20 parts per hundred of resin (phr) of LCBPP or POE was added into PP matrix. The blends of PP with LCBPP or POE were prepared by twin-screw extrusion. Injection molding process was used to produce PP foams using azodicarbonamide (ACA) as chemical blowing agent.

EXPERIMENTAL

Materials

Polypropylene homopolymer (PP) and branched polypropylene (LCBPP) with a melt flow index (MFI 230°C/2.16 kg) of 10 g/10 min and 3,5 g/10min, respectively, obtained from

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Braskem S.A. Brazil. Ethylene-octene copolymer (POE) with a melt flow index of 30 g/10 min obtained by Dow Chemical.

Sample preparation

PP with 20 parts per hundred (phr) of POE or LCBPP was obtained using a twin screw co-rotating extruder Coperion ZSK18 (screw diameter of 18 L/D = 38), operating at 200 rpm with constant feed ratio of 4 kg/h and temperature profile: 165- 170- 175- 175- 180- 185- 190ºC. The expansion process was performed in a Battenfeld injection molding machine. The mold employed contained a 115 mm x 55 mm x 7 mm cavity and the gate is located at center of the sample. A constant injection temperature at 200°C and a shut off nozzle was employed to produce the foam. Azodicarbonamide (ACA) was used as chemical blowing agent with amount fixed at 1.5 % and zinc oxide (0.5 %) was used as activator of ACA.

Analysis of foams

The apparent density of the foam was determined according to the standard method ASTM D3575. The scanning electron microscopy (SEM) was carried out to characterize the specimens' cell morphology using a Jeol JSM 6060. The samples were cut with liquid nitrogen. Quantitative measurements such as cell size and cell density were performed using an image analysis software (Image Tool). The cell density (N_0), which characterizes the number of cell per cm³ of foam was determined using the following equation [4] :

$$N_0 = \left({}^{n}/_{A}\right)^{\frac{3}{2}}\left(\rho_s/\rho_f\right) \quad (1)$$

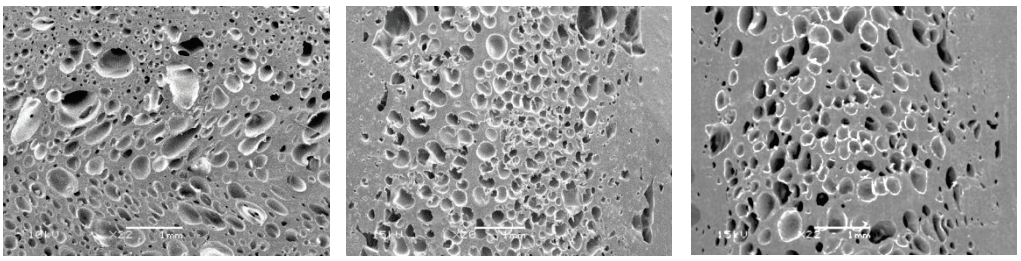
where n is the number of cells in the micrograph; A is the area of the micrograph (cm^2); ρ_s and ρ_f are the densities of the solid and the foamed material, respectively.

Dynamic-mechanical thermal analysis

The specimens for dynamic-mechanical thermal analysis (DMTA) testing were cut out from the injected plaques, and the testing was carried out using a TA Instruments Q800 DMA testing machine operation in a single cantilever for 12mm × 13.75mm × 7mm specimens. Strain was set at 0.02% with a frequency of 1 Hz and a temperature ramp of 3ºC/min. The scanning temperature test ramp ranged from −30 to 130°C. From the experimental data, the storage modulus (E'), Tg values and Tan δ were obtained.

RESULTS AND DISCUSSION

Typical foam micrographs of PP and the blends are shown in Figure 1. The Cell structure of the linear PP has a non-homogeneous size distribution and collapsing of the cells. It is known that branched polymers has higher expandability capacity [2, 3], in the case of the blends studied in this work, higher level of uniformity as well as reduction of collapsing effect occurred.



PP PP/LCBPP 100/20 PP/POE 100/20

FIGURE 1. SEM micrographs of PP, PP/LCBPP and PP/POE foams.

Image analysis through the software Image Tool allowed the determination of the cell size distribution of the different compositions tested[5]. The results of the image analysis of PP sample showed that up to 60% of the cells were in the size range between 50 and 100 microns while in the samples PP/LCBPP or PP/POE the values obtained are in the range of 45% and 42% respectively. Otherwise, the cell size distribution of the blends presented a higher homogeneous degree than PP, since 90% of the cells are in the site range of 50-200μm. The density measured for expanded PP was 0.48 $g.cm^{-3}$. The expanded blends showed increase in apparent density (Table 1). Taking into account the standard deviation of the analysis, there is an average increase of the 26% in the apparent density for the samples PP/POE and PP/LCBPP. As observed in morphological results, the addition of POE or LCBPP reduced the levels of expansion of the linear PP. The cell density results (cell/cm³) showed that the linear PP had higher cell density than the blends. The addition of LCBPP reduced the number of cells around -64% and in the sample with POE, -74%. Thus, the blend with branched polymers did not increase the cell density, otherwise increased the uniformity in cell size distribution. This effect is related by the improvement of the melt strength as well as the lower nucleation rate of the LCBPP or POE in the linear PP matrix [3, 6].

TABLE 1. Apparent Density of PP, PP/LCBPP and PP/POE foams.

Sample	Apparent Density ($g.cm^{-3}$)		Cell Density ($.10^3$ $cell.cm^{-3}$)
PP	0.48	±0.01	139
PP/LCBPP 100/20	0.64	±0.03	48.8
PP/POE 100/20	0.57	±0.05	36.1

The results of the dynamic-mechanical analyses, α and glass transition temperatures (Tg), storage moduli (E') and respective specific stiffness are presented in Table 2. The values of storage modulus, in term of the specific stiffness, showed variations which are dependent on the structure and the apparent density of the expanded samples studied.

Among the blends, the PP/POE sample showed the lowest specific stiffness due to the amorphous and flexible nature of POE [7]. The LCBPP used in this work has specific stiffness of about 178 $MPa.cm^{-3}.g^{-1}$, measured by the same technique, which increased the specific stiffness of PP/LCBPP blend.

TABLE 2. Results of the dynamic-mechanical analysis for PP and PP/branched polymers foams.

Sample	Storage Modulus		Tg	α transition
	23° (MPa)	Specific Stiffness ($MPa.cm^{-3}.g^{-1}$)	(°C)	(°C)
PP	77	160	4	77
PP/LCBPP	113	176	2	79
PP/POE	59	104	7	77

CONCLUSIONS

Linear expanded PP exhibited the largest cell density, however blending PP with ramified polymers resulted in decreasing of the cell density. Otherwise, the addition of 20 phr of the LCBPP or POE improved the cell size distribution due to the increase of the melt strength.
Dynamic–mechanical analysis of the foamed material revealed the behavior of the polymer added: in the case of the POE, increased the elastic behavior as well the use of the LCBPP increased stiffness.

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