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Effect of Long-chain Branching on the Foaming of Polypropylene with Azodicarbonamide

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ABSTRACT: In this article the influence of long-chain branching on the foaming behavior of polypropylene (PP) is investigated. Different branching contents are achieved by blending a linear PP (L-PP) and a long-chain branched PP (LCB-PP). Whereas, the L-PP does not exhibit any strain hardening in laboratory stretching experiments, blends with amounts of the LCB-PP higher than 2 wt% already show a pronounced strain-hardening behavior. The strain hardening increased with a growing amount of the long-chain branched PP. A laboratory scale foaming apparatus based on a capillary rheometer is developed for the foaming experiments. In foaming tests with azodicarbonamide as chemical blowing agent, a significant improvement of the foaming behavior with respect to a higher expansion ratio, a lower amount of connected cells, and a more homogeneous cell size distribution is found with increasing content of the LCB-PP up to a concentration of 50 wt%. At this concentration, the foaming behavior of the LCB-PP is reached. The results demonstrate that low amounts of long-chain branching can significantly improve the optimal foaming process of PPs with a chemical blowing agent, and that additions of the linear material up to 50 wt% to the LCB-PP do not have any influence on the favorable foaming performance of the long-chain branched PP.

KEY WORDS: linear polypropylene, branched polypropylene, blends, extensional rheology, chemical blowing agent, cellular structure.

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INTRODUCTION

Thermoplastic foams are widely used in the automotive, construction, and packaging industry. Although the market of foamed plastics is still dominated by polyurethane and polystyrene foams, polypropylene (PP) foams have gained growing interest. The PP has some properties which makes it especially suitable for foaming applications. The PP is a commodity polymer, has a comparably low density, relatively high service temperatures, a good impact resistance, and an excellent chemical resistance, especially in comparison to the main competitive polymers for foaming applications, namely polystyrene and polyethylene [1,2]. However, the foaming of conventional linear PPs in a continuous process is restricted by their rheological properties, especially their low melt strength [2]. Low viscosity and low melt strength lead to a rupture of the cell walls under the elongational forces occurring during cell growth. As a result, the final foam has a high amount of coalesced and open cells, which makes them unsuitable for many applications. A possibility to improve the foaming behavior of PPs is the incorporation of long-chain branches (LCB). The PPs with LCB exhibit a pronounced strain hardening behavior if elongated in the molten state, which is closely related to a higher melt strength [3]. Several studies have shown that foaming of long-chain branched PPs leads to higher volume expansion ratios, retarded cell coalescence, and a more homogeneous cell structure compared to L-PP. Phillips et al. [4] investigated the foaming behavior of a linear and a high melt strength PP using dichlorotetrafluoroethane (CFC 114) as the blowing agent. Whereas, for the linear PP the cellular structure collapsed due to rupture of the cell walls, a foam with a homogenous cellular structure and significant lower density could be produced using the PP with the high melt strength. Park and coworkers performed intensive studies on the development of extruded PP foams with a very low density and a fine cell structure [2,5–8]. Extremely large density reductions up to 90% could be achieved by foaming of a LCB-PP under optimized processing conditions. The density reduction of L-PPs was much lower because of severe cell coalescence. Similar results have been obtained by Michaeli et al. [9].

First investigations on blends of linear and long-chain branched PPs have been made by Spitaler and Macosko [10] and Reichelt et al. [11]. It was found that the foaming behavior of the L-PP with physical blowing agents like CO₂ or n-butane could already be improved with respect to higher expansion ratios, reduced cell coalescence and higher cell densities by an addition of LCB-PP in the order of 20–30 wt%.

Whereas, most of these investigations focus on the foaming behavior of linear and long-chain branched PPs, from a more practical point of view, only little fundamental knowledge about the dependency of the foaming behavior on rheological properties of the PP melt is available. Particularly, relationships between elongational flow and foaming are of great interest, as foaming is strongly influenced by elongational properties of the melt. Spitael and Macosko [10] investigated the influence of the strain hardening on foaming of L-PP and LCB-PPs with carbon dioxide as the blowing agent. They did not find, however, any direct correlation between the strain hardening and the cell concentration or the density reduction. Nevertheless, they could show that the cellular structure of the foams is caused by a combined influence of a higher number of nuclei of the linear blend partner and the reduction of cell coalescence due to strain hardening of the long-chain branched blend partner. Michaeli et al. [9] investigated the elongational behavior of an L-PP and a LCB-PP and combinations of the two by biaxial stress/strain measurement with a membrane inflation rheometer in order to assess the foamability of these polymers. They found a qualitative correlation between the stress-strain curves and the foam structure of the extruded sheets for the branched and the linear PP grades. Unfortunately foaming experiments of the blends of the linear and long-chain branched PP were not described.

The objective of this study is to investigate the effect of long-chain branching on the behavior of PPs foamed with azodicarbonamide. Opposite to the physical blowing agents used in most of the studies on the foaming behavior of PPs in the literature, azodicarbonamide is a chemical blowing agent. The density reduction achieved with chemical blowing agents is significantly lower compared to physical blowing agents. But there are certain technical advantages of chemical blowing agents, which make the study of this process worthwhile. Thus, one aim of this study is to investigate if the positive effect of long-chain branching on the foaming behavior with physical blowing agents reported in literature can be achieved by foaming with chemical blowing agents.

Another goal is to investigate in which way the foaming can be predicted from rheological experiments and to find guidelines on how to get an optimal material from existing products. Therefore, PPs with varying amounts of long-chain branching were prepared by blending an L-PP and an LCB-PP. Shear and extensional viscosity measurements were performed with the intention of establishing correlations between rheological properties and foaming.

MATERIALS AND METHODS

Materials

For this study, the commercial linear PP Moplen HP520H and the commercial long-chain branched PP Profax PF-814, both supplied by Basell Polyolefines, were used. The melt flow index (230°C; 2.16 kg) is 2 g/10 min for the linear PP (L-PP) and 3 g/10 min for the LCB-PP. The density at room temperature is 0.9 g/cm³ for both the PPs.

Blends of the two PPs with 2, 5, 10, 25, 50, and 75 wt% of LCB-PP were prepared in a co-rotating twin screw extruder. The extrusion was conducted at a temperature of 220°C and a rotational speed of 30 rpm. The blended components were subjected to the same procedure. To avoid a degradation of the molecules during the blend preparation, 1000 ppm of the stabilizer Irganox HP2215 were added.

Materials Characterization

The characterization of the PPs with respect to molar mass distribution and long-chain branching was carried out by high temperature size-exclusion chromatography (SEC), coupled with a multi-angle laser light scattering (MALLS) device and a refractive index (RI) detector. This method allows a determination of the absolute mass average molar mass and the radius of gyration of each SEC-fraction. A more detailed description of the analytical equipment used is given by Gabriel and Münstedt [12].

Shear rheological measurements were performed using a rotational rheometer with a plate-plate geometry of 25 mm in diameter and a gap of 1.5 mm under nitrogen at 180°C. Cylindrical samples of a thickness of 2 mm and a diameter of 25 mm were prepared in a hot press at a temperature of 180°C. Mechanical dynamic experiments over an angular frequency range of $0.01 \text{ s}^{-1} < \omega < 100 \text{ s}^{-1}$ were carried out using an Advanced Rheometric Expansion System (ARES) instrument manufactured by Rheometric Scientific. The ARES was also used for start-up tests at a shear rate of 0.01 s^{-1} .

Uniaxial elongational experiments were performed using a versatile version of an oil bath extensional rheometer that has been described in detail by Münstedt et al. [13]. A cylindrical sample is stretched vertically in a silicone oil bath, the density of which matches with the density of the molten PP as closely as possible. Constant strain rate experiments at a temperature of 180°C were run with several elongational rates between 0.01 and 1.0 s^{-1} . The samples for the uniaxial elongation

experiments were prepared by extrusion of the polymer melt through a capillary at a temperature of 180°C. Afterwards the extruded strands were annealed in a silicone oil bath to eliminate residual stresses.

Even though biaxial stretching is the main mode of deformation during cell growth in the foaming process, investigations in the literature primarily focus on uniaxial extensional viscosity. The main reason lies in the non-availability of reliable techniques to measure the biaxial elongational viscosity. However, a qualitative correlation between the strain hardening behavior in uniaxial and biaxial flow was found for LDPE [14]. To prove that such a correlation was also valid for the PPs, the biaxial elongational viscosity of the L-PP and the LCB-PP used in this investigation was measured utilizing a lubricated squeezing extensional flow rheometer (Iwamoto Setsakusyo Co., Ltd., Japan). An overview of this method has been reported by Takahashi et al. [15]. Disc shaped samples of a diameter of 25 mm and a height of 5 mm were prepared by compression molding. To achieve a uniform biaxial deformation and to prevent the shear deformation, silicone oil was applied as a lubricant to the upper and lower plates of the instrument and the sample. The viscosity of the silicone oil was in a range in which no additional extensional stresses for the samples occurred. Test with constant biaxial strain rates between 0.01 and 0.5 s⁻¹ were run at a temperature of 180°C.

Foaming

To analyze the foaming behavior a laboratory scale foaming apparatus based on a capillary rheometer was constructed. A schematic sketch of the apparatus is shown in Figure 1. The main parts of the apparatus are the piston, the cylinder, the capillary die, and the shut-off needle. The shut-off needle can be opened or closed by a hydraulic cylinder. A capillary die with a diameter of 1 mm and a length of 15 mm was used for all the experiments performed.

As there is no mixing unit attached to the foaming apparatus, the chemical blowing agent was added to the PPs in an internal mixer. For this investigation, a concentration of 2 wt% azodicarbonamide was used in all the experiments. The azodicarbonamide LUVOPOR ABF/70 P-FF supplied by Lehmann & Voss & Co was used without any additional modifier or accelerator. Azodicarbonamide decomposes around 200°C. The gas yield was about 220 cm³/g and the generated gas was mainly nitrogen, but also small amounts of carbon dioxide, carbon monoxide, and ammonia gas were released. In order to prevent decomposition of the chemical blowing agent azodicarbonamide during the mixing

Figure 1. Schematic sketch of the foaming apparatus.

process, the blending was performed at a temperature of 170°C and a screw speed of 15 rpm. The prepared mixture was put into the cylinder of the foaming apparatus and heated up to a temperature of 200°C. A pressure in the order of 150 bar inside the cylinder was generated by driving the piston down in order to keep the decomposed gas in solution. After a melting time of 5 min at the feeding temperature, the cylinder was cooled down to the foaming temperature, which was varied in the experiments between 180 and 160°C, at an approximate cooling rate of 2°C/min. Due to the melting time of 5 min and the low cooling rate, the total time from feeding the material to the foaming apparatus until the beginning of the foam extrusion is at least 15 min, which is sufficiently long to achieve a homogenization of the dissolved gas in the polymer melt by diffusion. During the cooling process, the pressure inside the cylinder was kept constant by adjusting the piston. When the foaming temperature was reached, the shut-off needle was removed and the material was pushed through the capillary die with a defined speed of 0.5 mm/s corresponding to an apparent shear rate of $D = 383 \text{ s}^{-1}$. In addition, experiments with a lower feeding temperature of 180°C were performed.

The volume expansion ratio of the foams produced was determined as the quotient of the density of the unfoamed polymer and the foam. The densities were measured using the buoyancy method. Foamed samples were fractured in liquid nitrogen, and scanning electron microscope images of the surfaces were taken. The cell structure was analyzed using an image analysis software (LeicaQWin). To determine the cell

diameter, the area of the fracture surface of the cells was measured by marking the contour of the cell. From the measured area, the diameter was calculated assuming a circular shape of the cells. The average cell diameter was determined by measuring at least 50 cells of three different samples at the minimum. The same images were used to measure the cell density. For the determination of the cell density, a frame with a defined area A was drawn in the image by the software and the number of cells n in the frame was counted. The ratio of the counted number of cells and the area of the frame in square centimeters describes the number of cells per square centimeter of the foamed polymer. In the literature [e.g., 5, 10] the cell density of polymer foams is defined as the number of cells per cm^3 of the unfoamed polymer N_0 :

$$N_0 = \left(\frac{n}{A}\right)^{3/2} \frac{\rho_0}{\rho_f} \quad (1)$$

where ρ_0 is the density of the unfoamed polymer, ρ_f is the density of the foam.

RESULTS AND DISCUSSION

Molecular Analysis

The results of the molecular analysis are shown in Table 1. The L-PP has a significantly lower mass average molar mass M_w and a smaller polydispersity M_w/M_n compared to the LCB-PP. For the blends, an increase of the molar mass and the polydispersity with growing amount of LCB-PP was found.

Table 1. Molecular data of the polypropylene blends [16].

Sample	M_w^a (kg/mol)	M_n^b (kg/mol)	M_w/M_n
L-PP	456	117	3.9
2 wt% LCB-PP	470	117	4
5 wt% LCB-PP	483	117	4.1
10 wt% LCB-PP	503	115	4.3
25 wt% LCB-PP	612	127	4.8
50 wt% LCB-PP	777	127	6.1
75 wt% LCB-PP	975	127	7.7
LCB-PP	1157	133	8.7

^aMass average molar mass determined by SEC-MALLS.

^bNumber average molar mass determined by SEC-MALLS.

Figure 2. Dependence of the root mean square radius of gyration $(s^2)^{1/2}$ on the molar mass M_{LS} [16].

In Figure 2 the mean square radius of gyration is plotted as a function of the molar mass. The compact line indicates the dependence of the radius of gyration on the molar mass, as found for a series of L-PP. As can be seen, the curves of the L-PP and the blend with 2 wt% LCB-PP follow the line for L-PP. For the other blends and the LCB-PP, a deviation of the radius of gyration to lower values is found. This is an indication for the presence of LCB. The stronger the deviation from the line for L-PP, the higher is the amount of long-chain branching. Thus, from Figure 2 it can be concluded that the amount of long-chain branches increases with growing LCB-PP content, as expected.

Rheological Characterization

The dynamic shear viscosities of the two blend partners and of the blends with 25, 50, and 75 wt% LCB-PP are shown in Figure 3. The shear viscosity of the L-PP is higher compared to the LCB-PP within the frequency range measured. The viscosities of the blends are between the values of the two blend partners within a wide range of frequencies and follow a logarithmic mixing rule, as could be shown in [16]. Thus, it can be assumed that the L-PP and the LCB-PP are miscible.

Figure 3. Dynamic shear viscosities $|\eta^*(\omega)|$ of the L-PP, the LCB-PP and the blends with 25, 50, and 75 wt% LCB-PP [16].

Whereas, at the lowest measured frequency, the viscosities of the blends and the L-PP are almost the same, the difference between the samples is more pronounced in the high frequency region from 1 to 100 s^{-1} .

In Figure 4 the elongational viscosities of the L-PP and the LCB-PP in uniaxial (Figure 4(a)) and equibiaxial (Figure 4(b)) elongation are shown. For the L-PP, no strain hardening occurs. The overshoot of the curves above the linear viscoelastic curve found for the L-PP at low strain rates in biaxial elongation is probably caused by experimental inaccuracies and is also found for other linear polymers [17]. For the LCB-PP, a pronounced strain hardening occurs at all strain rates tested in uniaxial as well as in equibiaxial elongation. The slope of the curves in the region of strain hardening is lower in biaxial elongation, and thus the enhancement of the viscosity above the linear viscoelastic curve is less pronounced. Nevertheless, there exists a qualitative correlation between the uniaxial and the biaxial flow concerning the strain-hardening behavior of PPs.

The uniaxial elongational viscosity of three of the blends is shown together with the curves of the two blend partners in Figure 5. The blend with 2 wt% LCB-PP already exhibits a slight strain hardening at low strain rates, although no LCB could be detected by light scattering. This is an indication for the high sensitivity of elongational rheology to

Figure 4. (a) Uniaxial elongational viscosities $\eta_{E,\text{uniaxial}}$ and (b) biaxial elongation viscosities $\eta_{E,\text{biaxial}}$ of the L-PP and the LCB-PP as a function of the time t at different strain rates $\dot{\epsilon}_0$. The full lines represent the threefold and the sixfold of the linear start-up viscosity in shear $\eta_0^+(t)$, respectively.

the existence of LCB as the polydispersity of the two materials is similar (Table 1). The blends containing 10 wt% LCB-PP or more show strain hardening for all strain rates tested, which gets more pronounced with increasing amounts of LCB-PP. Figure 5 indicates that low amounts of a long-chain branched material added to an L-PP lead already to a pronounced strain hardening. A more detailed discussion about the relationship between the molecular structure and the rheological properties of the investigated PP blends can be found in a previous paper by the authors [16].

Figure 5. Uniaxial elongational viscosities $\eta_{E, \text{uniaxial}}$ of PP blends as a function of time t at different strain rates $\dot{\epsilon}_0$.

In the foaming process the applied strain rates are in the order of 1 s^{-1} , and Hencky strains of 3–4 are typical [18]. That is why a closer look will be taken at the elongational behavior at the highest measured Hencky strain rate of 1 s^{-1} , which is close to the condition occurring in the foaming process.

For a more quantitative estimation of the strain hardening effect, the so-called strain hardening coefficient S was determined. It is defined as the ratio between the elongational viscosity at a distinct time and the linear elongational start-up viscosity at the same time. In Figure 6, the strain hardening coefficient is shown as a function of the LCB-PP content at strain rate of 1 s^{-1} and a total Hencky strain of 2.7. While for the blend containing 2 wt% LCB-PP, no strain hardening is found at this strain rate, the blend containing 5 wt% LCB-PP already shows a strain hardening coefficient larger than 1. A nearly linear increase of the strain hardening coefficient with increasing percentage of LCB-PP is found under the given conditions.

Foaming Behavior

In Figure 7 the expansion ratio of the foamed strands is shown as a function of the LCB-PP content for three different foaming temperatures. The expansion ratio of the LCB-PP is significantly

Figure 6. Strain hardening coefficient S at a Hencky strain rate $\dot{\epsilon}_0$ of 1 s^{-1} and a Hencky strain ϵ_H of 2.7 as a function of the LCB-PP content.

Figure 7. Expansion ratio as a function of the weight proportion of the LCB-PP $\phi_{\text{LCB-PP}}$ at three different foaming temperatures T (feeding temperature $T_0 = 200^\circ\text{C}$, extrusion velocity $v = 0.5 \text{ mm/s}$).

Figure 8. Scanning electron microscopy images of fracture surfaces of foams of: (a) the L-PP; (b) the blend containing 5 wt% LCB-PP; (c) the blend containing 50 wt% LCB-PP; and (d) the LCB-PP foamed at a temperature of 160°C (feeding temperature $T_0 = 200^\circ\text{C}$, extrusion velocity $v = 0.5\text{ mm/s}$).

higher compared to the L-PP at all measured temperatures. For the blends, a nearly linear increase of the expansion ratio with increasing amount of LCB-PP is found up to 25 wt%. Between 25 and 50 wt%, the increase of the expansion ratio is reduced, whereas the blends with 50 wt% or more exhibit an expansion ratio which is similar to that of the pure LCB-PP.

As can be seen from Figure 7, an increase of the expansion ratio with decreasing foaming temperature was found for all the samples. This increase can be explained by a reduction of gas loss due to the lower diffusion coefficient, a higher nucleation rate due to the higher pressure drop, and a faster stabilization of the cellular structure as the difference between the foaming and the crystallization temperature is reduced.

To understand the differences in the expansion ratios of the blends, the cellular structure of the extruded foams is analyzed at the lowest foaming temperature of 160°C. In Figure 8, scanning microscopy images of the fractured surfaces of the L-PP, the blends containing 5 and 50 wt% LCB-PP, and the neat LCB-PP are shown. For the L-PP (cf. Figure 8(a)) a very inhomogeneous cellular structure with a broad

Figure 9. Cell diameter and cell density as a function of the LCB-PP content at a foaming temperature of 160°C (feeding temperature $T_0 = 200^\circ\text{C}$, extrusion velocity $v = 0.5\text{ mm/s}$).

variety of different cell sizes is visible. Especially in the center of the strand, a high amount of unfoamed polymer matrix is found. Open cell walls and connected cells are visible. The foam of the blend containing 5 wt% LCB-PP (Figure 8(b)) clearly shows a more homogeneous cell size distribution. The amount of unfoamed polymer matrix is reduced, but open cell walls and connected cells are still visible. In the case of the blend containing 50 wt% LCB-PP (Figure 8(c)), a rather homogeneous cell size distribution is visible, and the average cell size is larger compared to the L-PP and the blend containing 5 wt%-LCB-PP. Unfoamed polymer matrix is no more visible, and the rupture of cell walls is widely prevented. The homogeneity of the cellular structure of the blend containing 50 wt% LCB-PP and the neat LCB-PP (Figure 8(d)) is very similar. However, the cells of the LCB-PP are larger.

To have a more quantitative comparison of the cellular structure, the average cell diameter and the number of cells per area of the foam were determined by image analysis. The results are shown in Figure 9 as a function of the LCB-PP content. The foam of the L-PP shows the smallest cell size, which increases with increasing amounts of LCB-PP. Despite the smaller cell size of the L-PP, the cell density of the L-PP is similar to that of the LCB-PP. This can be explained by the high amount of gas loss of the linear PP, due to the low melt strength. With increasing

amounts of LCB-PP the cell density runs through a distinct maximum at around 50 wt-% LCB-PP. A higher cell density of blends from an L-PP and LCB-PP compared to the blend components was also found by Spital and Macosko [10], and might be referred to a combined influence of a higher nucleation rate of the linear blend component and a higher melt strength of the long-chain branched blend component.

As the solid moieties of the decomposition of the chemical blowing agent act as a nucleation agent for the formation of gas bubbles a heterogeneous nucleation process takes place. The number of nuclei and the nucleation rate are mainly determined by the distribution of the nucleating particles within the polymer melt, the pressure drop at the die of the foaming apparatus and the surface tension of the polymer melt [2]. From investigations on linear and long-chain branched polyethylenes, it is known that the influence of LCB on the surface tension of the melt is very small [19]. Thus, there is no evidence that the long-chain branching of the LCB-PP should have any influence on cell nucleation. From microscopy images of fracture surfaces of unfoamed samples filled with 2 wt% azodicarbonamide, no inhomogeneity of the distribution of the azodicarbonamide particles inside the PP matrices was found. Nevertheless, the presence of further additives in the PPs, which might also act as nucleation agents, cannot be excluded, as both the PPs used are commercial grades. Thus, it is very likely, that the L-PP contains a higher number of heterogeneous nucleation sites due to additives in the commercial products, which differ in kind and amount between the L-PP and the LCB-PP¹. Because of the higher shear viscosity of the L-PP the pressure drop at the die of the L-PP (105 bar) is 10–15 bar higher than the pressure drop of the LCB-PP (90 bar). Due to the larger pressure drop, the nucleation rate of the L-PP is higher, and a larger number of cells is nucleated for the L-PP compared to the LCB-PP. It has to be mentioned, that because of the low solubility of nitrogen, which is the main gas released by the decomposition of the azodicarbonamide, and because of the low pressure drop rate due to the die length of 15 mm, a part of the gas is going out of solution before leaving the die. This so-called premature foaming has an influence on the cell nucleation in a way that the nucleation rate is reduced and a broader distribution of the final cell size is caused. Because of this, the obtained cell diameters of the extruded foam strands are significantly larger compared to cell

¹From a chemical analysis using FTIR-spectroscopy hints to the existence of nucleating agents could not be found, however.

sizes in the order of 10 μm achieved by foam extrusion with higher soluble blowing agents like CO_2 and shorter dies [2,10].

A higher nucleation rate and a higher number of nucleated cells of L-PP in comparison to LCB-PP have also been reported in the literature. Park and Cheung [2] studied the nucleation behavior of L-PP and LCB-PP and found that the L-PP had a higher nuclei density. A definite explanation for the different nucleation behavior of L-PP and LCB-PP is not given in the paper, but effects of additives and impurities in the polymer matrix are mentioned as possible factors. A higher nucleation rate of an L-PP in comparison to two different LCB-PP was also reported by Spitael and Macosco [10]. Differences in the crystallization kinetics between the L-PP and LCB-PP are discussed as the main reason for the higher number of nucleated cells in the foam of the L-PP. The LCB-PP showed the onset of crystallization 10°C higher than the L-PP. According to the authors, the start of crystallization at a higher temperature forces the blowing agent out of the melt due to a lower solubility of gas in the crystalline regions, so that it is no more able to contribute to nucleation.

Although it cannot be excluded completely, the reduction of the nuclei density due to an earlier onset of crystallization is very unlikely to occur in the present experiments. This is mainly because the cooling of the extruded strands by the surrounding air after leaving the die is comparably slow, and the cell nucleation takes place immediately after the die exit. In addition, the added chemical blowing agent is acting as a nucleation agent for crystallization so that the onset of crystallization of the L-PP is only 5°C lower than that of the LCB-PP used in the present investigation, as could be shown by DSC measurements of the PPs filled with 2 wt% of the azodicarbonamide under a pressure of 30 bar and a cooling rate of 10 K/min. Thus, it is more likely that the higher nucleation rate of the L-PP is caused by a combined influence of a slightly higher pressure drop and a higher number of heterogeneous nucleation sites in comparison to the LCB-PP.

Despite the higher nucleation rate of the L-PP, it shows a significantly lower expansion ratio in comparison to the LCB-PP and most of the blends. A difference in the gas available for the expansion between the L-PP and the LCB-PP can be excluded, as the amount of chemical blowing agent added was the same for all PPs, and there are no differences in the decomposition behavior of the azodicarbonamide in the L-PP and the LCB-PP, as was shown by thermoanalysis. Thus, the main reason for the lower expansion ratio of the L-PP is a higher gas loss to the environment during the foaming process. Due to the low melt strength of the L-PP, the elongational forces during the cell growth

process can lead to rupture of cell walls. Because of the rupture of cell walls, cells coalesce and a high amount of connected cells occur. Fewer cell walls lead to a larger gas loss to the environment because, due to the connected cells, the diffusion of gas from the center of the strand to the surface becomes easier. Besides the reduction of the expansion ratio, the gas loss can cause the collapse of already formed cells if all the gas inside a cell is lost to other cells or to the environment. Thus, it is very likely that the high amount of unfoamed material in the foamed strand of the L-PP (Figure 8(a)) is caused by cell collapse. In the case of the LCB-PP, the pronounced strain hardening prevents the rupture of cell walls during the expansion so that the gas loss can only be caused by diffusion through the walls of the closed cells. Due to the higher resistance to diffusion, less gas is lost to the environment and a higher expansion ratio, in comparison to the L-PP, is reached. The strong increase of the expansion ratio between 5 and 50 wt% LCB-PP can be related to the increased strain hardening (Figure 6). The increasing amount of strain hardening leads to a stabilization of the cells so that they can grow to a larger size before the rupture of cell walls occurs. This is also the reason for the increase of the cell density with increasing amount of LCB-PP up to 50 wt%. For the blends with more than 50 wt% LCB-PP, cell rupture was mostly averted, which means that due to the pronounced strain hardening, the melt strength was high enough to prevent a failure of the cell walls by the occurring elongational forces during the expansion process. Because of this, the expansion ratio of these blends is similar to that of the LCB-PP. The decrease of the cell density for the blend with 75 wt% LCB-PP in comparison to the blend with 50 wt% LCB-PP, however, is caused by the influence of the lower nucleation rate of the LCB-PP.

Influence of Feeding Temperature

In a second set of experiments, the feeding temperature at which the material was put into the foaming apparatus was reduced to 180°C. In Figure 10 the expansion ratio at a foaming temperature of 160°C is compared for the two different feeding temperatures. As can be seen, the expansion ratio of the foams produced with the feeding temperature of 180°C is much lower compared to the results for a feeding temperature of 200°C. The main reason for the lower expansion ratio at a feeding temperature of 180°C is probably a lower amount of gas available for foaming. It is assumed that in the case of $T_0 = 180^\circ\text{C}$, the decomposition of the azodicarbonamide is not completed, whereas at the higher feeding temperature of 200°C, the chemical blowing agent decomposed

Figure 10. Expansion ratio as a function of the LCB-PP content at the foaming temperature of 160°C for two different feeding temperatures T_0 (extrusion velocity $v = 0.5\text{ mm/s}$).

completely, and the maximum amount of gas is obtained². Although the differences in the expansion ratio between the two feeding temperatures are more pronounced at higher LCB-PP contents, a qualitatively similar dependency of the expansion ratio on the amount of LCB-PP is found for both feeding temperatures. The expansion ratio shows a pronounced increase up to 50 wt% LCB-PP, and for the blends with 50 wt% or more, a behavior similar to that for the LCB-PP is found. The significantly higher differences in the expansion ratio between the two feeding temperatures for the blends with high amounts of LCB-PP compared to the blends with low amounts of LCB-PP can be explained by the high gas loss of the blends with low amounts of LCB-PP. Due to the weak melt strength of these blends, most of the additional gas available for foaming at the higher feeding temperature is lost to the environment by the enhanced gas diffusion through the ruptured cell walls.

²In thermoanalysis it was found that the foamed strands obtained with a feeding temperature of 180°C still contained azodicarbonamide which did not decompose during the foaming experiment, which was not the case for the strands foamed with a feeding temperature of 200°C .

Figure 11. Cell diameter and cell density as a function of the LCB-PP content at a foaming temperature of 160°C (feeding temperature $T_0 = 180^\circ\text{C}$, extrusion velocity $v = 0.5 \text{ mm/s}$).

Whereas, the dependency of the expansion ratio on the LCB-PP content is at least qualitatively similar for the two different feeding temperatures, the dependency of the cell diameter and the cell density on the amount of LCB-PP at $T_0 = 180^\circ\text{C}$ is different from that of $T_0 = 200^\circ\text{C}$. This can be seen by a comparison of Figures 9 and 11. The lower feeding temperature leads to significantly lower cell diameters and much higher cell densities for all PP samples. Opposite to the findings for the feeding temperature of 200°C , the L-PP shows the largest cell diameter at $T_0 = 180^\circ\text{C}$ (Figure 11). By increasing the amount of LCB-PP up to 50 wt% the cell diameter is reduced and the cell density increased. For the blends with 50 wt% LCB-PP or more a very similar cellular structure is found.

The significantly higher cell density for a feeding temperature of 180°C compared to 200°C is an indication of an improved cell nucleation. As the decrease of the feeding temperature has no significant influence on the pressure drop³, the better nucleation behavior at a feeding temperature of 180°C is probably caused by a different effect of the

³Due to the lower amount of gas dissolved in the polymer melt in case of a feeding temperature of 180°C the pressure drop is 10–20 bar higher.

azodicarbonamide on the cell nucleation. For the foams produced with a feeding temperature of 200°C, only the solid moieties remaining after the decomposition process contribute to the cell nucleation as inactive nucleation agents, i.e., they do not generate gas anymore. As the decomposition of the azodicarbonamide is not completed during the melting at 180°C there are still not any, or only partly, decomposed azodicarbonamide particles in the matrix when the material is extruded through the die which can act as active nucleation agents. Active nucleation agents are defined as products which decompose during the foam extrusion and release a gas [20]. In the case of $T_0 = 180^\circ\text{C}$, it is not unrealistic to assume that the decomposition of a part of the azodicarbonamide is taking place during the extrusion through the die caused by the pressure drop and the local temperature increase due to shear heating. Therefore, one can imagine that the bubble formation starts directly at the azodicarbonamide particles leading to a higher number of nucleated cells and smaller cell diameters.

The change of the dependency of the cell diameter and the cell density on the amount of LCB-PP by reducing the feeding temperature from 200 to 180°C can also be explained by the influence of the different nucleation behavior. In the case of feeding at 180°C the cell nucleation is dominated by the active nucleation effect of the azodicarbonamide, which may be similar in the L-PP and the LCB-PP. Therefore, a similar nucleation behavior for the two blend partners and all of the blends should be expected. Thus, the differences in the cellular structure shown in Figure 11 are caused by effects occurring during the cell growth. The higher cell diameter and the lower cell density of the L-PP in comparison to the LCB-PP are caused by cell coalescence due to the low melt strength of the L-PP. The increase of the cell density with a growing amount of LCB-PP from 2 to 50 wt% is referred to as a reduction of the cell coalescence due to the increasing strain hardening.

CONCLUSIONS

Rheological properties and the foaming behavior of blends from an L-PP and an LCB-PP have been investigated. By molecular analysis, it was shown that the molar mass, the polydispersity, and the amount of long-chain branching increase with growing amount of LCB-PP. The LCB-PP has a lower shear viscosity compared to the L-PP in the high shear rate region, which is relevant for the foaming process and shows a pronounced strain hardening in elongational flow. A qualitative correlation between the strain hardening in uniaxial and biaxial elongation was found for the two blend partners, which allows a

discussion of the foaming process with predominantly biaxial deformation using the results of the rheological characterization in uniaxial flow. It was shown that the addition of less than 10 wt% LCB-PP already leads to a significant strain-hardening behavior, which is more pronounced at lower strain rates. This is an indication that the rheological behavior in elongational flow reacts very sensitively on the presence of long-chain branching. An almost linear increase of the strain hardening with a growing amount of LCB-PP was found at the highest measured strain rate of 1 s^{-1} , which is in the order of strain rates occurring in the foaming process.

In foaming tests with azodicarbonamide as chemical blowing agent, a significant increase of the expansion ratio of L-PP was found by the addition of LCB-PP between 5 and 50 wt%. This is attributed to a lower amount of gas loss to the environment, as the increased melt strength, due to the strain-hardening behavior, reduces the rupture of cell walls during the cell growth process. For blends with 50 wt% LCB-PP or more, a similar expansion ratio compared to the LCB-PP was found, although the strain-hardening behavior further increases with the LCB-PP content. This leads to the conclusion that under the conditions of the foaming experiments in this investigation, a certain amount of strain hardening is already sufficient for an optimized foaming behavior.

For a feeding temperature of 200°C , large cell sizes with average cell diameters of several hundred micrometers and low cell densities were found for all PPs tested. The L-PP showed a lower cell size than the LCB-PP, but a similar cell density. Whereas, the cell size increases with increasing amount of LCB-PP, the cell density shows a distinct maximum around 50 wt% LCB-PP. The increase of the cell size and the cell density up to 50 wt% LCB-PP can be explained, by a reduction of cell coalescence and cell collapse due to the increased melt strength. The reduction of the cell density at high amounts of LCB-PP is referred to as a lower nucleation rate of the LCB-PP in comparison to the L-PP, which is mainly caused by the lower pressure drop of the LCB-PP.

By a reduction of the feeding temperature from 200 to 180°C , the cell sizes could be reduced significantly and the cell densities increased, because, due to the incomplete decomposition of the chemical blowing agent, the azodicarbonamide particles act as active nucleation agents. But, as the decomposition of the azodicarbonamide is not complete at $T_0 = 180^\circ\text{C}$, a lower amount of gas is available for foaming leading to a significant decrease in the expansion ratio. Besides that, at $T_0 = 180^\circ\text{C}$, pronounced differences between the foams of the L-PP and the LCB-PP were observed. The foamed strands of the L-PP exhibit a lower expansion ratio, a larger cell size, and lower cell density than the

LCB-PP, which is referred to the lower melt strength of the L-PP leading to cell coalescence and open cells. For the blends, an increase of the cell density combined with a decrease of the cell size was found with an increasing amount of LCB-PP up to 50 wt%, which is explained by the reduction of cell wall rupture due to the increased melt strength.

The results presented demonstrate that long-chain branching has a positive influence on the foaming behavior of PP with azodicarbonamide. A high density reduction, a homogeneous cell size distribution and a low amount of connected cells are the most striking effects. It could be shown that the blending of low amounts of LCB-PP to L-PP is an appropriate way to improve the foaming behavior of L-PP with azodicarbonamide.

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