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Elongational Viscosity and Foaming Behavior of PP Modified by Electron Irradiation or Nanotube Addition

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Summary: In this study, two different routes were chosen which are expected to influence the elongational viscosity and, thus, the foaming behavior of polypropylene (PP). Electron irradiation of a linear PP was performed at room temperature using different doses. Enhanced long-chain branching was observed with increased irradiation dose. In addition, a linear PP was filled with 5 wt% multiwalled carbon nanotubes (MWNT) by melt mixing at 200 °C. These modified PP materials were investigated with respect to their shear and elongational behavior. After foaming, irradiated PP led to an expansion factor which is about 60% higher than that of the non-irradiated product. In case of PP filled with 5 wt% MWNT the value of the expansion factor is about 70% higher than that of pure PP expanded under the same conditions. The cell structure is much finer in both cases as compared to unmodified PP.

Keywords: carbon nanotubes; elongational viscosity; foaming behavior; polypropylene; radiation

Introduction

It is known that polymer foaming is strongly influenced by the elongational melt viscosity. In previous studies it was demonstrated that long-chain branched polypropylenes showing a strain hardening behavior lead to higher volume expansion ratios, retarded cell coalescence and a more homogeneous cell structure compared to linear PP.[1–3]

In this study, two different routes to modify the elongational viscosity and, thus, the foaming behavior of conventional linear PP were chosen. On the one hand, a commercial linear polypropylene was treated by electron beam irradiation of different doses.[4] This irradiation leads to long-chain branching and strain hardening. On the other hand, a linear PP was filled with multiwalled carbon nanotubes (MWNT). Above the electrical percolation concentration, where a nanotube network is formed, a conductive foam is expected to be formed. In addition, an enhancement in viscosity should favor the formation of small homogeneous cells and due to the nanotube network formation an enhanced stability of cell walls may be assumed.

The effect of the two different modifications on the rheological behavior of the polypropylene in shear and especially in elongational flow was analyzed. Foaming tests were performed on selected samples at temperatures of 170 °C and 180 °C using a laboratory scale foaming apparatus based on a capillary rheometer (Figure 1).[1] The foam structures were characterized.

Irradiation of Polypropylene

The isotactic polypropylene homopolymer (Novolen PP H2150 from Basell Polyolefins, PP1) with a melt flow index of 0.3 g/10 min (230 °C, 2.16 kg) and a density at room temperature of 0.90 g/cm^3 was irradiated with 1.5 MeV electrons using an electron beam accelerator of the type ELV-2

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Table 1.
Molecular data of irradiated PP1 (from SEC-MALLS measurements).[6]

Sample	dose [kGy]	M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	M_w/M_n [–]	λ[a)]
PP1-0	0	160 000	669 000	1 654 000	4.2	n. d.
PP1-5	5	126 000	473 000	1 135 000	3.8	n. d.
PP1-60	60	74 000	285 000	874 000	3.8	0.44

[a)] λ... number of long chain branches per 1000 monomer units (n. d. - not detectable).

(Budker Institute of Nuclear Physics, Russia). The irradiation was carried out under a nitrogen atmosphere at atmospheric pressure in a special vessel with 5 and 60 kGy.[5] After irradiation two annealing steps were added as described in [5]. Molecular data as determined by SEC-MALLS are shown in Table 1.

As seen on the PP1-60 sample, electron beam irradiation leads to long-chain branching, whereas the molecular weight decreased due to chain scission. The polydispersity does not change significantly due to irradiation. Crystallization temperatures and crystallinity of the three samples are similar.[6]

It is well known that the foaming behavior is strongly connected to the melt rheological properties of the matrix material. A low viscosity and low melt strength lead to a pronounced cell coalescence resulting in large and connected cells and relatively low expansion rates. Therefore, shear and elongational viscosities were determined for the PP materials. The results obtained at 180 °C are shown in the Figure 2 and 3.

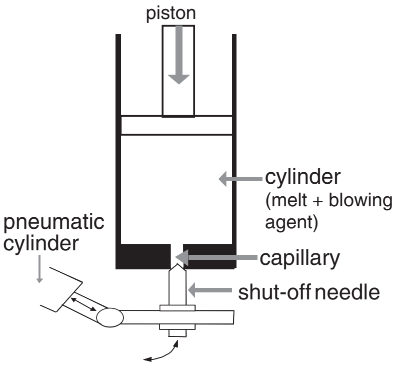

Figure 1.
Schematic of the foaming apparatus based on a capillary rheometer.

The shear viscosity was determined by oscillatory tests using an ARES rheometer with plate-plate geometry [5], the elongational viscosity was measured using an oil bath uniaxial extensional rheometer of the design by Münstedt (e.g. [7]).

From Figure 2 it follows that the irradiation reduces the shear viscosity at 5 kGy only slightly, however at 60 kGy significantly. This is in accordance with the molecular weight reduction. A decrease in viscosity can be observed in elongation, too, as the linear part of the curve follows the threefold value of the linear start-up viscosity in shear $\eta_0^+(t)$ for all three polyolefins (Figure 3). The irradiation with only 5 kGy already leads to a strain hardening effect which is more pronounced at 60 kGy irradiation dose.

Foaming tests were performed at 170 °C and 180 °C. As chemical blowing agent 2 wt% azodicarbonamide was premixed with the irradiated PP material using an internal mixer. The foaming procedure is described in detail in [1]. The piston speed was 0.5 mm/s corresponding to a shear rate of $D = 383\ s^{-1}$.

The expansion ratio was calculated using the density of the polymer divided by the density of the foam. The results are illustrated in Figure 4. In general, the expansion ratio is higher at lower expansion temperature. Already at 5 kGy irradiation dose a significant increase in expansion ratio can be observed which becomes still larger at higher irradiation dose. At 60 kGy

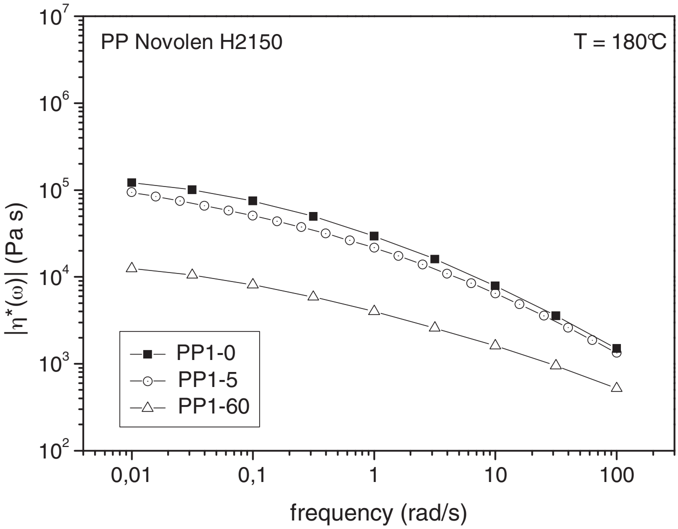

Figure 2.
Dynamic shear viscosity $|\eta^*(\omega)|$ of the neat PP1 and the two samples irradiated with 5 kGy and 60 kGy

irradiation dose the expansion factor at 170 °C is about 60% higher than that of the non-irradiated product.

The foamed samples were cryofractured in liquid nitrogen and surfaces were investigated using scanning electron microscopy. The images shown in Figure 5 illustrate the cellular structure of the foams obtained at 180 °C foaming temperature. As it is seen, pure PP1 contains a lot of cells but also a high amount polymer matrix material which was not foamed. The material irradiated at 5 kGy leads to a quite inhomogeneous foam structure. Next to quote small cells, big cells and also unfoamed material is observed in the SEM analysis. For PP irradiated at 60 kGy a comparatively homogeneous cell structure can be observed. The

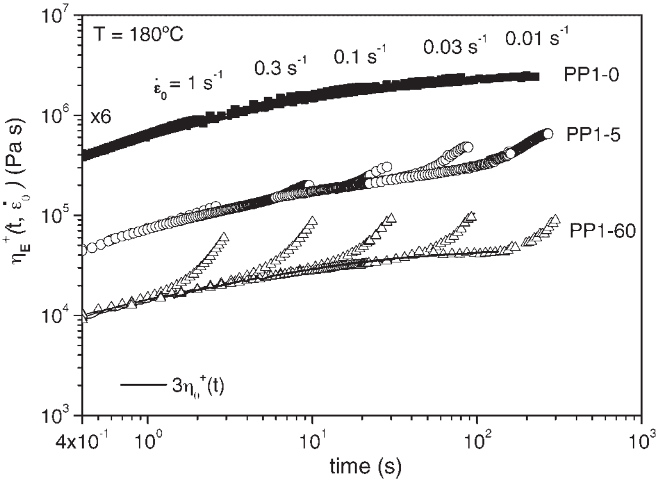

Figure 3.
Elongational viscosity $\eta_E^+(t)$ of the neat PP1 and the two samples irradiated with 5 kGy and 60 kGy at different strain rates ε_0.

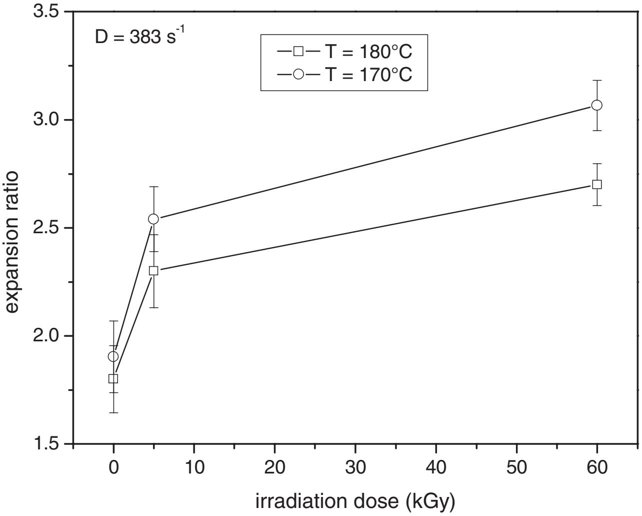

Figure 4.
Expansion ratio of PP1 at foaming temperatures of 170 °C and 180 °C.

cells are closed and not connected indicating that the pronounced strain hardening behavior enhances the stability of the cell walls. Despite the lower shear viscosity of this sample as compared to pure PP the foaming behavior is enhanced illustrating

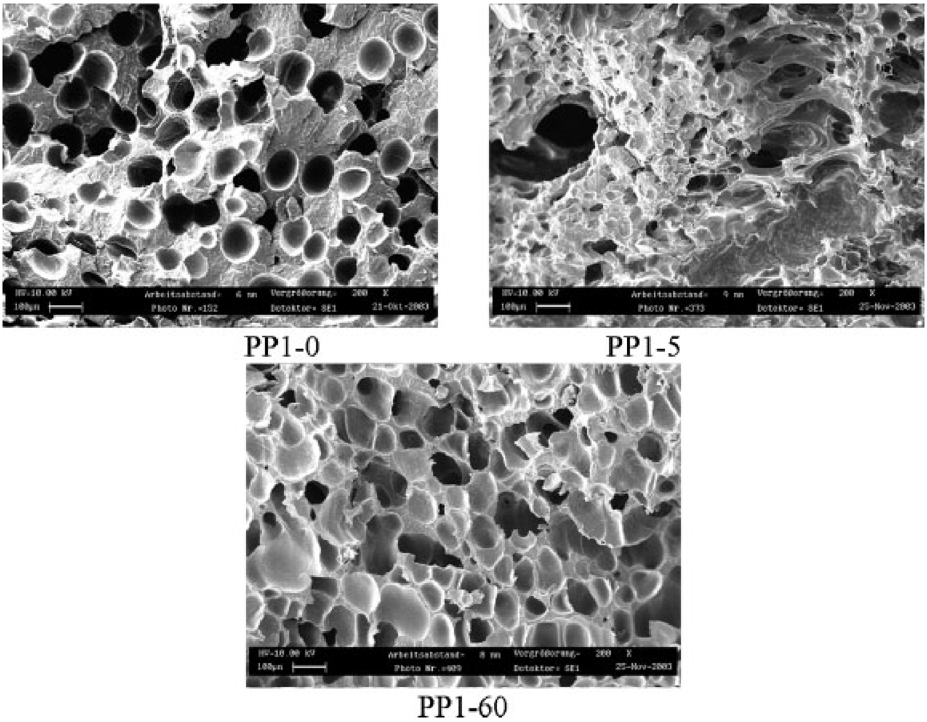
PP1-0
PP1-5
PP1-60

Figure 5.
SEM images of cryofractured surfaces of foams of PP1 prepared at T = 180 °C and D = 383 s^{-1} with 2 wt% azodicarbonamide, scale bar 100 μm.

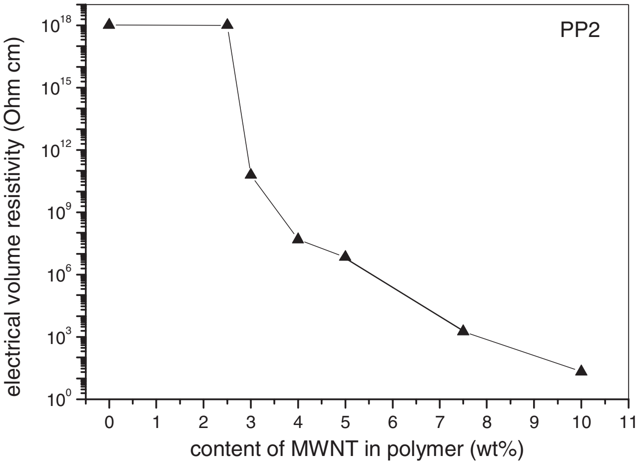

Figure 6.
Electrical volume resistivity of PP2-MWNT composites (on pressed plates).

the stronger influence of the foaming behavior on melt elongational properties and especially on the strain hardening behavior than on shear viscosity.

Polypropylene with Multiwalled Carbon Nanotubes

Polypropylene Moplen HP 520 H (Basell Polyolefins, PP2) with a melt flow index of 2 g/10 min (230 °C, 2.16 kg) and a density at room temperature of 0.90 g/cm^3 was melt mixed with thin crude multiwalled carbon nanotubes (MWNT) supplied from Nanocyl S.A., Belgium. According to the supplier the MWNT have diameters in the range between 10 and 25 nm and a purity of >80%.

In the first step, the electrical percolation composition was studied by varying the amount of MWNT incorporated into PP2. Melt mixing was performed using a DACA microcompounder (conical twin-screw compounder with bypass, capacity 4.5 cm^3) at 200 °C, 50 rpm mixing speed and 15 min mixing time. The extruded material was pressed at 200 °C into thin sheets of 0.35 mm thickness in order to measure the electrical resistivity. This was performed on the sheets using a Keithley 8009 Resistivity Fixture for high resistive samples and on small strips (30 mm × 2 mm) cut from the sheets using a four point measurement cell

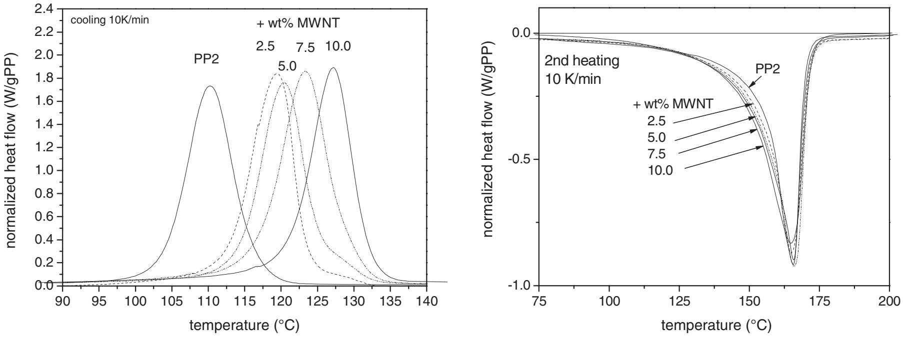

Figure 7.
Crystallization and melting behavior (second heating) for MWNT filled PP2.

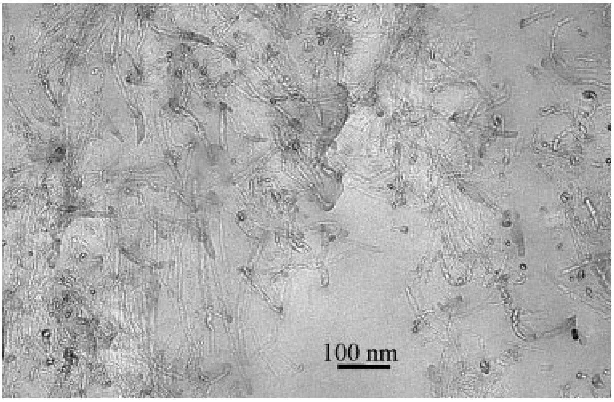

Figure 8.
Transmission electron micrograph of the sample of PP2 with 5 wt% MWNT.

for low resistive samples, both combined with an electrometer 6517A (Keithley). The obtained percolation curve is shown in Figure 6 illustrating that the electrical percolation starts between 2 and 3 wt% MWNT. From 5 wt% upwards the material shows electrical resistivities lower than 10^7 Ohm cm and can be assigned as moderately conductive materials according to ASTM D 4496 standard.

The nanotubes incorporation also influences the crystallization behavior, whereas the melting behavior is not changed much (see Figure 7). The melting enthalpy is slightly enhanced (from 98.5 J/g to 104.6 J/g at 5 wt% MWNT). The crystallization temperature is increased by nearly 17 K at 10 wt% MWNT addition and by about 11 K at 5 wt% MWNT. Thus, during the foaming process solidifying can start already in earlier stages possibly preventing cell coalescence.

For the foaming experiments the sample with 5 wt% was selected and prepared in a larger amount. Transmission electron microscopy on ultrathin sections as shown

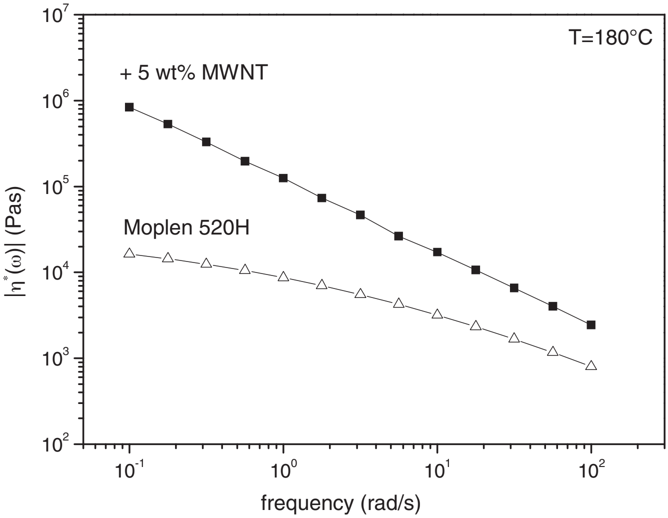

Figure 9.
Dynamic shear viscosity $|\eta^*(\omega)|$ of PP2 and the composite with 5 wt% MWNT.

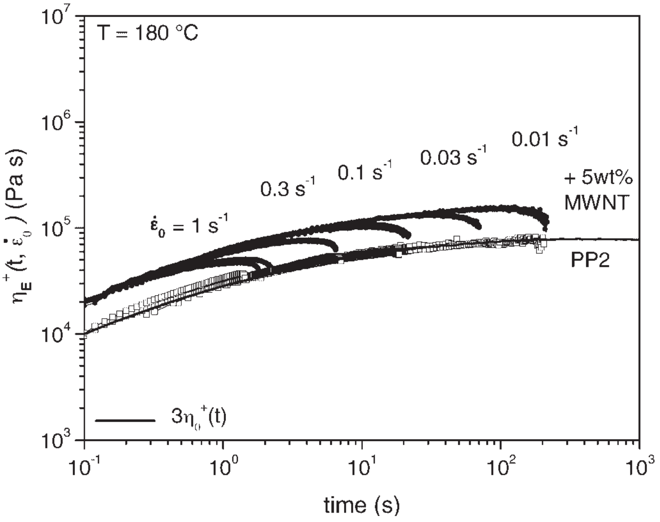

Figure 10.
Elongational viscosity $\eta_E^+(t)$ of PP2 and the composite with 5 wt% MWNT at different strain rates ε_0.

in Figure 8 illustrate that the nanotubes are quite well dispersed even if areas with higher and lower nanotube concentrations may be observed.

The composite with 5 wt% MWNT was investigated with respect to its shear and elongational behavior as shown in Figure 9 and 10 for a measuring temperature of

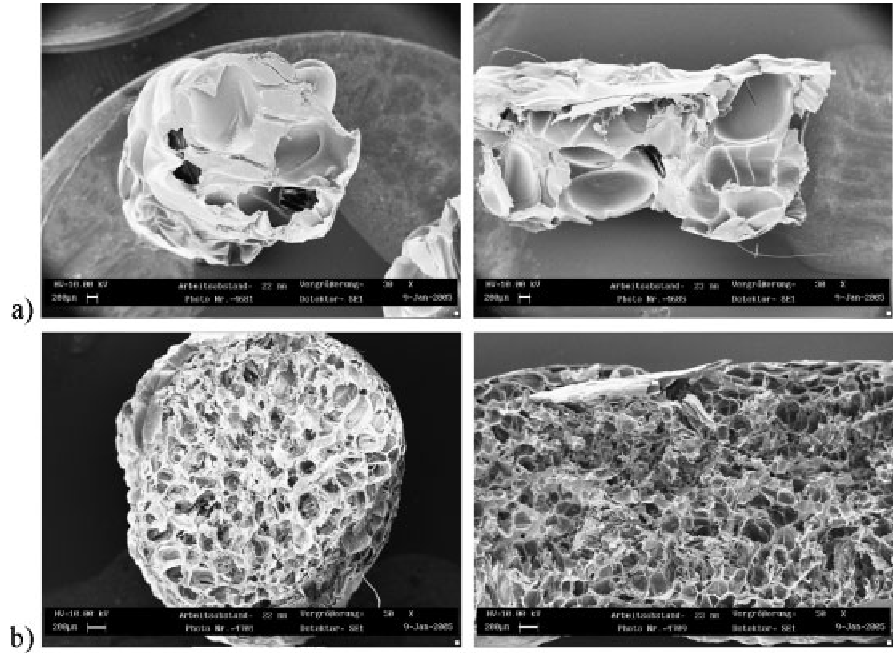

Figure 11.
SEM images of cryofractured surfaces of foams prepared at T = 170 °C, D = 730 s^{-1} with 2% CO$_2$ as physical blowing agent, a) neat PP2, b) PP2 with 5 wt% MWNT (left: perpendicular, right: parallel) to the extrusion direction, scale bar 200 μm.

180 °C. As described in detail in [7], for the elongational tests defined strands have to be prepared by melting the nanocomposite material again. During this procedure the extrudate swell was investigated which was reduced from 0.68 for PP2 to 0.17 for PP2 with 5 wt% MWNT.

Compared to the electron beam irradiation, the addition of nanotubes enhances the melt viscosity significantly. The frequency dependence is nearly linear in the double logarithmic scale, thus reflecting the network structure of MWNT within the PP2 matrix.

An enhanced viscosity is also observed in elongation. However, no strain hardening effect could be observed, but strain softening occurs. It has to be mentioned that a constriction of the strands during deformation was found. Therefore, the maximum Hencky strains applied were only about 1.5 compared to 2.5 for pure PP2.

With respect to the application potential of MWNT filled PP it is interesting to investigate whether the foaming behavior is improved by the filler.

The chemical blowing agent azodicarbonamide could not be used as it was not possible to mix it in at temperatures below its decay. Therefore, the foaming of the nanotube filled polypropylene had to be performed by a physical blowing agent. For this purpose, polypropylene together with dry ice was put into the cylinder of the foaming apparatus. The amount of dry ice was chosen to achieve an approximate content of 2 wt% CO_2, which dissolved in the molten polypropylene inside the foaming apparatus due to the elevated pressure caused by the compression of the mixture in the cylinder by the piston. Foaming was performed at 170 °C using a piston speed of 1 mm/s corresponding to an apparent shear rate of $D = 730\ s^{-1}$. The expansion ratio of PP2 was found to be 3.6 at 170 °C, that one of the nanocomposite with 5 wt% MWNT was 6.0. This increase of about 70% is comparable to that of the irradiated PP1.

The cell structure as observed from cryofractures performed perpendicular and parallel to the foamed strand direction (see Figure 11) exhibits much smaller and more homogeneous cells than the pure PP.

Thus, an improved foaming behavior was found although no strain hardening could be obtained for this sample. This finding has to be related to the generally higher viscosity of the MWNT-filled PP. As shown in[2] on unfilled polypropylenes, higher melt viscosity leads to higher expansion ratios due to the slower diffusion of released gas through the expanded strand and enhanced melt strength. In addition, for the MWNT filled PP it has to be taken into account that the increased crystallization temperature effects a solidification of the foam already at earlier stages. Together with the nanotubes located in the cell walls the crystallinity contributes to a stiffness of the walls reducing their expansion and making their fracture more difficult, thus reducing coalescence.

Conclusion

It was shown that different concepts with respect to material modification lead to an enhanced foaming behavior of polypropylenes. On one hand, electron beam irradiated PP resulted in higher expansion ratios, smaller cell sizes, and improved cell homogeneity due to long-chain branching. As the melt viscosity was reduced due to molecular mass reduction, the pronounced strain hardening is the reason for the good foaming behavior.

For a nanocomposite containing 5 wt% MWNT but showing no strain hardening an improved foamability was found, too. This can be assigned to the higher viscosity level leading to an enhanced melt strength, and following from that to more stable cells, and a reduction in gas loss through open cell walls. In addition, the crystallization is shifted to higher temperatures, resulting in a solidification of the sample and a stabilization of the cell walls at a comparably earlier stage of the foaming process.

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