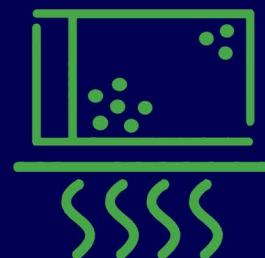




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INFLUENCE OF PROCESSING CONDITIONS ON THE APPEARANCE OF BEAD FOAMS MADE OF THE ENGINEERING THERMOPLASTIC POLYBUTYLENE TEREPHTHALATE (E-PBT)

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Abstract

While the established bead foams expandable polystyrene (EPS) and expanded polypropylene (EPP) are commonly produced batchwise by suspension polymerization and in autoclave processes, respectively, a method that is usually applied for novel bead foams is the continuous foam extrusion coupled with an under-water granulator (UWG). One advantage thereof is that additives can be incorporated very easily. Anyhow, besides the temperature and pressure regime of the extruder, further process parameters can be varied such as the throughput, water temperature etc. Consequently, this is a rather complex process, especially when chemical modifiers (e.g., chain extenders) are used. Within this study the influence of throughput, water temperature and talc concentration on the foam morphology of chemical modified polybutylene terephthalate bead foams (E-PBT) are shown. By adjusting the parameters properly, it is possible to achieve bead foams with a density of 85 kg/m³. Additionally, it could be proven by DMA measurements that E-PBT exhibits a higher temperature resistance than conventional bead foams.

Introduction

Considerable progress has been made in the development of novel bead foams during the last two decades [1]. Especially, sustainability, enhanced mechanical performance and thermal resistance are in the focus of industrial and academic research. The established bead foams – expandable polystyrene (EPS) and expanded polypropylene (EPP) – have a rather limited thermal resistance of 80 and 100 °C, respectively. Yet, the use of engineering thermoplastics is an approach to overcome this issue. Meanwhile, some works on polyethylene terephthalate (E-PET) [2], polyamide (E-PA) [3], polycarbonate (E-PC) [4] and polybutylene terephthalate (E-PBT) [5] exist. Usually, these beads are produced in a continuous process via a foam extrusion line coupled to an under-water granulator (UWG). However, processing these materials is not trivial, especially as chemical modifications have to be used to ensure sufficient expansion [6]. It is also known that these chemical modifications have big influence on the foam morphology and consequently on the mechanical behavior (e.g., compression strength).

However, the process itself is quite complex and requires adjustment of a lot of parameters, such as

throughput, extrusion temperature, water temperature and many more. Amongst others, it was found that several factors can be used to increase the pressure to achieve a lower foam density. Also, the water temperature in the UWG determines the appearance of the beads and - even more interestingly - the fusion quality. Particularly, the bead fusion of semi-crystalline foams is not fully understood yet. Crystallization effects on the surface are expected to play a crucial role [7].

An earlier work of Köppl et al. showed the influence of certain process and material parameters, respectively, on the expansion and the cell morphology of the beads. Different from this work, the use of chain extenders seems to be essential to improve the expansion and to achieve bead fusion in the steam chest molding process [5]. Reactions and the effects of the commercial chain extender Joncryl® were summarized in our previous review [6]. Also, further parameters like throughput and water temperature of the UWG were considered the first time.

This work highlights the influence of the processing setup on the appearance (cell morphology and sphericity) and the properties (i.e., crystallinity) of PBT bead foams.

Materials

In this study PBT Pocan B 1300 from Lanxess AG (Cologne, Germany) was modified with the epoxy-based oligomeric chain extender (CE) Joncryl® ADR 4468 from BASF SE (Ludwigshafen, Germany). The materials were processed on a Dr. Collin tandem line (Maitenbeth, Germany) with attached under-water granulator LPU from company Gala Kunststoff- und Kautschukmaschinen GmbH (Xanten, Germany) with settings according to our previous study [5]. However, in this study the throughput and water temperature were varied. Also, the addition of talc Mistrocell M90 from Imerys (Paris, France) as nucleating agent was investigated.

Fusion of the beads was carried out at Neue Materialien Bayreuth GmbH on a Teubert TVZ162/100PP (Blumberg, Germany) with high pressure steam supplied by a HaeCo II steam generator from Unibell (Hwaseong, South Korea).

Discussion

In an earlier work the optimum concentration of chain extender (CE) in terms of a high expansion and homogeneous cells was found to be 1 wt.-%. Keeping the amount of CE constant, the water temperature was set to

60 °C and the throughput was varied (6, 8 and 10 kg/h, respectively). The resulting foam morphologies are shown in Figure 1.

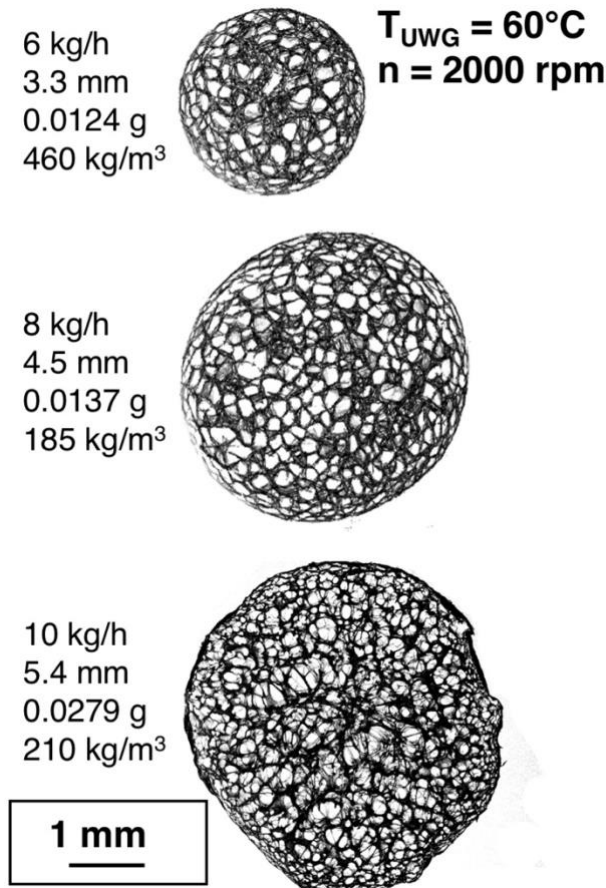


Figure 1: Foam morphologies of foamed beads produced with varying throughputs at a water temperature of 60 °C

Obviously, at the same knife speed of 2000 rpm more material is conveyed with increasing throughput. Consequently, the average weight and diameter of the beads increase. Unexpectedly, the increasing throughput does not lead to an ever growing expansion as one would expect a (beneficial) increase of the pressure. The bead density at the lowest throughput of 6 kg/h is 460 kg/m³ and thereby rather high, while with 8 kg/h the density is 185 kg/m³. The achieved cell sizes are similar (approx. 210 μm). At the lower throughput a smaller melt volume is pushed out, which get cooled much faster by the water in the UWG and the growing cells stabilize earlier. However, at 10 kg/h the bead density was 210 kg/m³. Reason for this is that the rotational speed of the B-extruder had to be adjusted to maintain a stable process. Thereby, the pressure prior to the foaming decreased from 205 bar (6 and 8 kg/h) down to 170 bar. It is well known, that the pressure drop governs the nucleation / expansion and a high pressure drop is beneficial [8]. Even though the beads produced with 10 kg/h have a larger average diameter, the density

reduction could not be improved. Furthermore, a shrunken surface and cell rupture was noted while at lower throughputs spherical beads with smooth surfaces were obtained. The observed shrinkage and cell rupture might be the result of the slower cooling of the larger melt volume hindering a sufficient cell stabilization.

Additionally, the crystallinity changes from 26.1 % (6 kg/h) to 28.6 % (8 kg/h) and 29.1 % (10 kg/h) as a larger melt volume tends to take longer to cool down and thus more time remains for crystallization.

The water temperature was increased up to 80 °C and the trials were repeated with throughputs of 8 and 10 kg/h, respectively. It has to be mentioned that the process runs much more stable with the higher water temperature.

The resulting foam morphologies of the beads are shown in Figure 2.

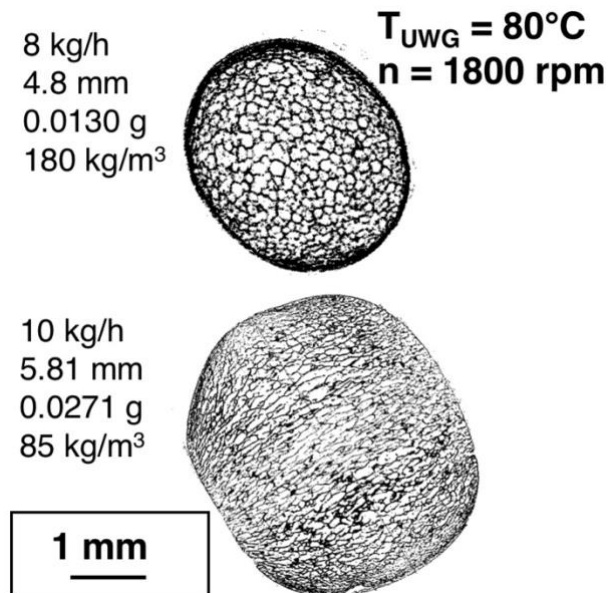


Figure 2: Foam morphologies of foamed beads produced with varying throughputs at a water temperature of 80 °C

The expansion at 8 kg/h is similar to the trials with the lower water temperature (60 °C) and a density of 180 kg/m³ was achieved. Anyhow, here it was possible to further reduce the density by increasing the throughput. Two effects have to be noted as (i) the increased water temperature would allow the melt to expand more as the stabilization will take place a little later and (ii) for this set up the melt pressure could be increased from initially 149 bar up to 187 bar with increasing throughput while maintaining a stable process. The morphologies of bead foams produced with systematically varied water temperature from 50 to 90 °C are shown in Figure 3.

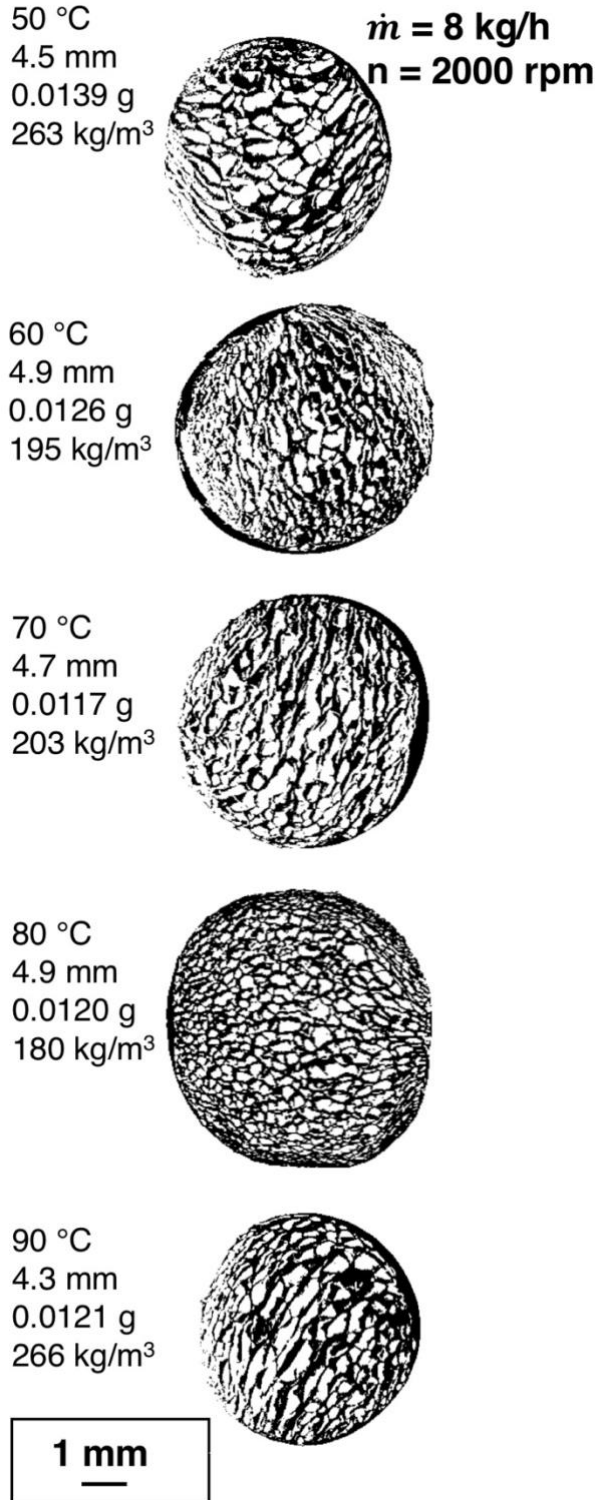


Figure 3: Foam morphologies of foamed beads produced with varying water temperatures from 50 to 90 °C at a throughput of 8 kg/h

It is worth to mention that the process runs unstable at the lowest and the highest water temperature resulting in undesired fluctuations. In the case of the lower temperatures, crystallization at the outlet of the UWG is

promoted, which would lead to hindered melt flow and even to partial or complete freeze of the holes of the UWG. On the other hand, at the high temperature of 90°C the water can be easily stimulated to boil while getting in contact with the polymer melt, which is the cause for process instabilities.

At the temperatures 60-80 °C (stable process) the obtained densities range from 180 to 200 kg/m³ while at the temperature of 50 and 90 °C (unstable process) higher densities of approx. 265 kg/m³ were noted. For the beads foamed at a water temperature of 50 °C significant larger cells can be seen which could be possibly explained by lesser nucleation and a higher melt elasticity due to the cooler environment.

As summarized by Okolieocha et al. [9] the heterogeneous nucleation plays an important role for improving the cell morphology of polymeric foams. For PBT extrusion foams the cell size could be decreased by the addition of slight amounts of supra-molecular additives down to 689 μm at a density of 80 kg/m³ [10]. However, more common is the approach to use talc as nucleating agent.

Therefore, trials were performed with talc as nucleation agent. The lowest direct dosable concentration was 0.15 phr. With increasing talc concentration, the process runs less stable. However, spherical beads were obtained.

In Figure 4 the influence of the addition of talc on the foam morphology of the bead foams can be seen. In this case, the cell sizes and cell size distribution cannot be significantly improved by the addition of talc.

First, the expansion is less compared to the corresponding samples without any talc. For all concentrations the density is above 250 kg/m³. Processing with talc also leads to slight process fluctuations, possibly because crystal nucleation is also promoted by the particles. Depending on the talc concentration the crystallization increases (0.15 phr: 27.3%, 0.2 phr: 29.0 %, 0.5 phr: 30.3 % and 1 phr: 32.1 %).

It has to be mentioned that the beads without any nucleation agents already show relative homogeneous cell morphology. In a previous work we could show cell sizes of 155 μm for PBT modified with 1 wt.-% CE [5]. Although, the cell size could be decreased by the addition of talc at the concentration of 0.2 and 0.5 phr, respectively, but at higher densities. Yet, even the concentrations are rather low their impact on the expansion is significant. It seems like flow behavior and/or crystallization behavior during the expansion at the outlet of the UWG is negatively influenced by the talc.

Yet, the worst appearance is noted for the highest talc concentration (i.e., 1 phr). It can be assumed that the melt flow behavior is rather impaired, most likely because crystallization increases the viscosity. Also, the presence of a high amount of particles in the cell walls act as defects during the cell growth resulting in coalescence and rupture.

Especially, in the outer area of the bead large cells are visible.

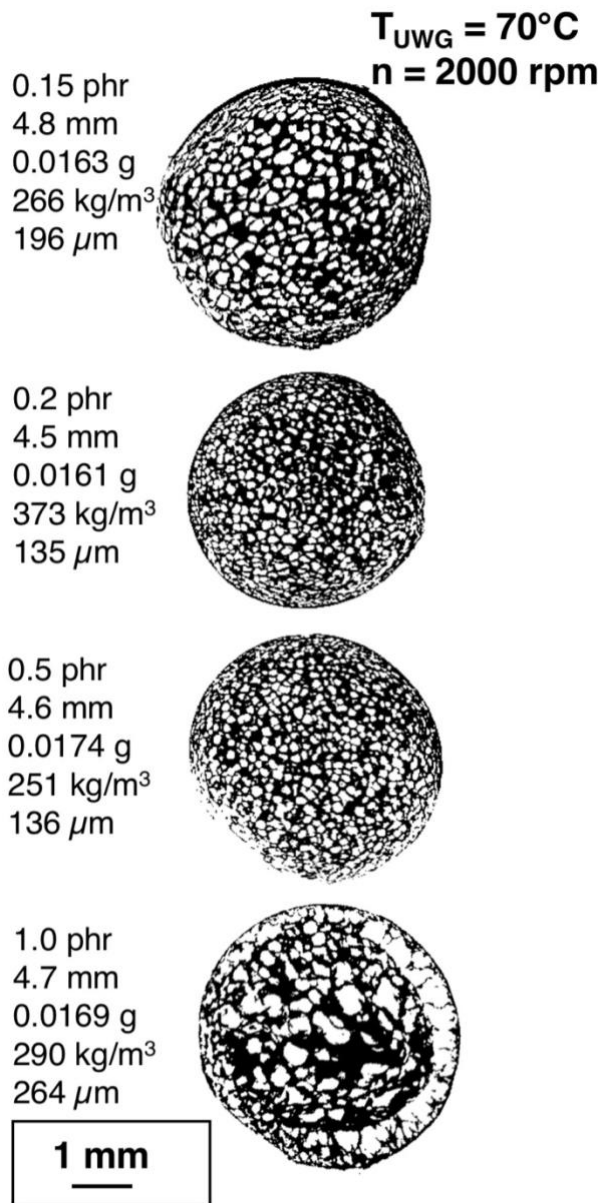


Figure 4: Foam morphologies of foamed beads produced with different amounts of talc

Beads made at a throughput of 10 kg/h and a water temperature of 80 °C (cf. Figure 2) were steam chest molded to plates and further characterized regarding the thermal resistance.

In general, engineering polymers exhibit higher service temperatures. While for compact materials the thermal resistance can be quantified by the heat distortion temperature (HDT, DIN EN ISO 75) or Vicat Softening temperature (VST, DIN EN ISO 306) there are no unified methods for foams. The only standard (DIN 53424) is meanwhile withdrawn. Alternatively, different methods were adapted and shown in the literature such as static compression tests at elevated temperatures [11,12], DMA

measurements [3,4] and evaluation of dimensional stability after oven treatments [13,14].

In Figure 5 the DMA curves of E-PBT (155 kg/m³) and EPP (160 kg/m³) are shown. E-PBT shows a slight shoulder at about 70 °C which corresponds to the T_g . In general, both curves are more or less overlapping up to 100 °C. However, $|E^*|$ of EPP decreases significantly at temperatures above 100 °C. The decrease is much less pronounced for E-PBT and the drastic loss of properties is recognizable above 200 °C. This indicates the higher temperature of E-PBT quite well. The material shows good dimensional stability up to 200 °C.

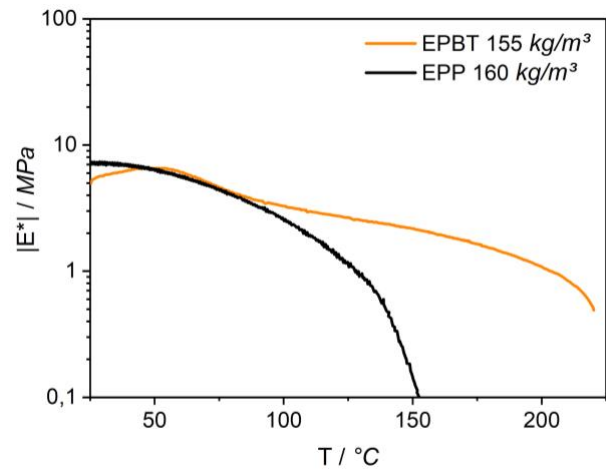


Figure 5: DMA curves of E-PBT and EPP with similar densities (155 kg/m³ and 160 kg/m³)

Conclusions

It can be concluded that the interaction of the different process- and material parameters is quite complex. The process stability is strongly dependent of the water temperature of the attached UWG. Rather low and high temperatures (50 and 90 °C, respectively) lead to unfavorable fluctuations. It was possible to achieve beads from chemical modified PBT (1 wt.-% CE) with a density of 85 kg/m³ by setting a throughput of 10 kg/h and a water temperature of 80 °C.

It is important to maintain a high pressure (i.e., by setting a high throughput) but also to consider other effects that hinder the melt flow during the expansion such as crystallization. The addition of talc does not lead to any significant improvement in terms of expansion and cell morphology.

By DMA measurement it could be shown that E-PBT exhibits a better performance under thermal load compared to a standard bead foam made from EPP. Up to approx. 200 °C the complex modulus only decreases slightly while EPP fails at a temperature below 150 °C.

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