

Evaluation of the Potential of Polybutylene Terephthalate / Poly(phenylene oxide) Blends for Bead Foam Production

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Abstract. An attempt to achieve bead foams that possess a higher thermal stability as well as an intrinsic flame retardancy is the use of suitable engineering polymers, such as the combination of polybutylene terephthalate (PBT) and poly(phenylene oxide) (PPE). However, both materials are very challenging to process – especially in the continuous foam extrusion coupled with an underwater granulator to obtain bead foams. In the recent study we show how the PBT/PPE blend morphology is affected by the PPE content and an epoxy-based chain extender (CE). Also, the morphologies of the bead foams with different blend compositions are shown. Stable processing was possible up to a PPE content of 10 wt.-%. The crystallization behavior changes by the addition of PPE and the lowest bulk density for the foamed beads was 130 kg/m³. This study aims to understand the melt behavior of PBT/PPE blends and to evaluate its potential for bead foam application in a continuous process. By using an epoxy-based chain extender the blend morphology can be influenced and a fine and homogeneous distribution of PPE in PBT can be achieved. The beads could be fused seamlessly with the rather novel radiofrequency technology. Trials with a cone calorimeter revealed a lesser (peak) heat release when burning compared to bead foams made from expanded polypropylene (EPP).

INTRODUCTION

A lot of development in the field of bead foams can be recognized within the last two decades [1]; this concerns mainly the establishment of novel polymers with higher functionality compared to the classic bead foams (i.e., expandable polystyrene, EPS and expanded polypropylene, EPP) to enable a broader field of applications. Up to now, bead foams with increased sustainability (e.g., from polylactide), enhanced mechanical properties (e.g., from thermoplastic polyurethanes) or higher thermal resistance (e.g., from engineering and high-performance polymers) have been described. The latter also sometime come along with an improved flame resistance (e.g., polyetherimide). However, often engineering polymers (polyesters such as polybutylene terephthalate or polyethylene terephthalate) are used, which lead to higher service temperatures but have an unfavorable burning behavior. Moreover, the low melt strength of these materials is not beneficial for processes like foaming. Reactive extrusion with suitable chemical modifiers can help to overcome this issue as reported by Jeong et al. [2]. In recent works we could show the influence of an epoxy-based chain extender on the melt viscosity and influences of different processing parameters on the expansion behavior of PBT [3]. PBT bead foams (E-PBT) possess a high potential for applications that require an elevated service temperature. It was shown that the resistance to deformation under thermal load is very high compared to bead foams made from polystyrene (PS) or polypropylene (PP) respectively [4]. Still the burning behavior needs to be improved for certain applications [5].

Besides the addition of flame retardants [6], a possible strategy to improve the burning behavior is to create blends with intrinsic flame-retardant polymers. PPE – poly(phenylene oxide) – is one possible material for this. Due to its complex melt flow behavior the processing is not trivial. Yet, the combination of PPE and PS could be established in a commercial product; namely expandable bead foams which possess an improved burning behavior (i.e., UL94 rating V0) at low densities [7].

As the engineering polymers have higher melting points than the established polymers that are used for bead foams, the fusion process which is commonly carried out with a steam chest molding machine is much more challenging as

higher steam temperatures are required. Consequently, unconventional high steam pressures and specialized equipment are needed. Though, most recently, steamless alternatives for the fusion of the beads are getting more interesting [1]. These are promising in terms of materials and components that are sensitive to water (e.g., electronic integrational parts) or when processing polymers that require high steam temperatures such as engineering polymers. One of these techniques is the use of radiofrequency.

EXPERIMENTAL

Materials

For this work PBT Pocan B1300 from Lanxess AG (Cologne, Germany), PPE powder Noryl 640 from Sabic (Geleen, Netherlands) and chain extender (CE) Joncryl ADR 4468 from BASF SE (Ludwigshafen, Germany) were used. Bead foams were prepared by means of a Dr. Collin tandem (Maitthenbeth, Germany) line with an attached under-water granulator from Gala Industries (Xanten, Germany). Supercritical CO₂ (Rießner-Gase GmbH, Lichtenfels, Germany) was injected as blowing agent. The procedure is similar to the process described in our previous work [3]. The beads were fused using a Wave Foamer from company Kurtz GmbH & Co. KG (Kreuzwertheim, Germany) which works with radiofrequency (RF). While voltage, welding time and tool pressure were adjusted individually the radiofrequency was set with 27.12 MHz. The plates had a dimension of 300 x 200 x 30 mm.

Characterization

The melt viscosity was determined using an RDA III rheometer from TA Instruments Inc. (New Castle / DE, USA) at 250 °C on round melt-pressed samples (diameter of 25 mm) and a plate distance of 1 mm.

TEM measurements were carried out to analyze the blend morphology on a transmission electron microscope Zeiss/LEO EM 922 Omega (Oberkochen, Germany). The samples had a thickness of 50 nm. No staining was necessary as both polymers showed a good contrast. The foamed beads were investigated by SEM. Therefore, the sputter-coated surfaces of cryo-fractured beads were analyzed by a scanning electron microscope JEOL JSM-6510 (Akishima, Japan). An acceleration voltage of 10 kV was used.

Burning tests based on the standard ISO 5660-1-2002 were conducted with a cone calorimeter iCone from Fire Testing Technology Ltd. (East Grinstead, United Kingdom). For the test samples with a size of 100 x 100 x 30 mm were cut out of the fused plates. Sample distance to the ignition coil was 25 mm and an incident heat flux of 35 kW/m² was set.

RESULTS AND DISCUSSION

PBT/PPE Blends

Figure 1 shows the frequency sweeps of PBT/PPE blends and the neat polymers without and with added chain extender.

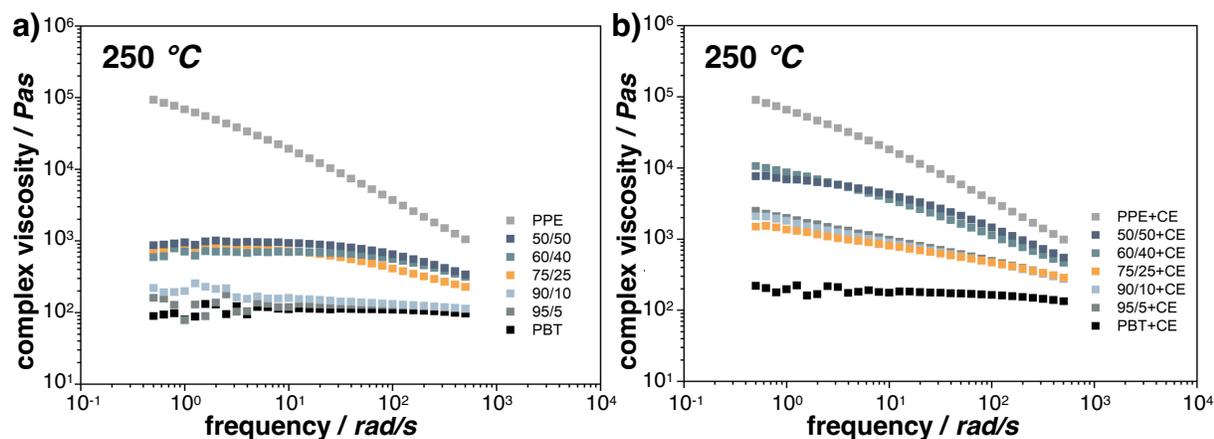


Figure 1: Frequency sweeps of PBT/PPE blends with different PPE contents at 250 °C. a) without CE. b) with CE.

While the neat PBT has a very low viscosity the one of neat PPE is extremely high, resulting in difficult melt processing behavior. The blends can be found in between both curves of the neat polymers. When adding CE the viscosity of PBT and the blends increases and the curves do not show a linear plateau anymore. Likely branched or even crosslinked chain structures are formed due to the reaction with the CE. It seems like PPE itself is not reacting with the epoxy groups of the chain extender – what agrees to the literature [8]. The CE usually can react with carboxy and hydroxy groups, while carboxy is even favored [9]. PPE does not owe these kinds of functional groups; therefore the reaction of the chain extender can be expected to be selective with the PBT only. The curve of PPE with CE shows also a slightly lower viscosity than neat PPE (without CE); here the CE that is not reacting with the polymer could act more like a lubricant in the melt.

In Figure 2 the TEM images of PBT/PPE blends can be seen. It is an immiscible blend. The darker areas are PBT while the lighter areas are PPE domains. The blend morphology is mainly governed by the high viscosity differences of both polymers [10]. The lower viscous PBT forms the matrix and entraps smaller domains of PPE. Interestingly the droplet size of the PPE domains decreases about up to 85% when adding the chain extender. The CE seems to act as a compatibilizer between PBT and PPE [8]. This is also described in the literature [9] for other polyesters, such as PLA and PET.

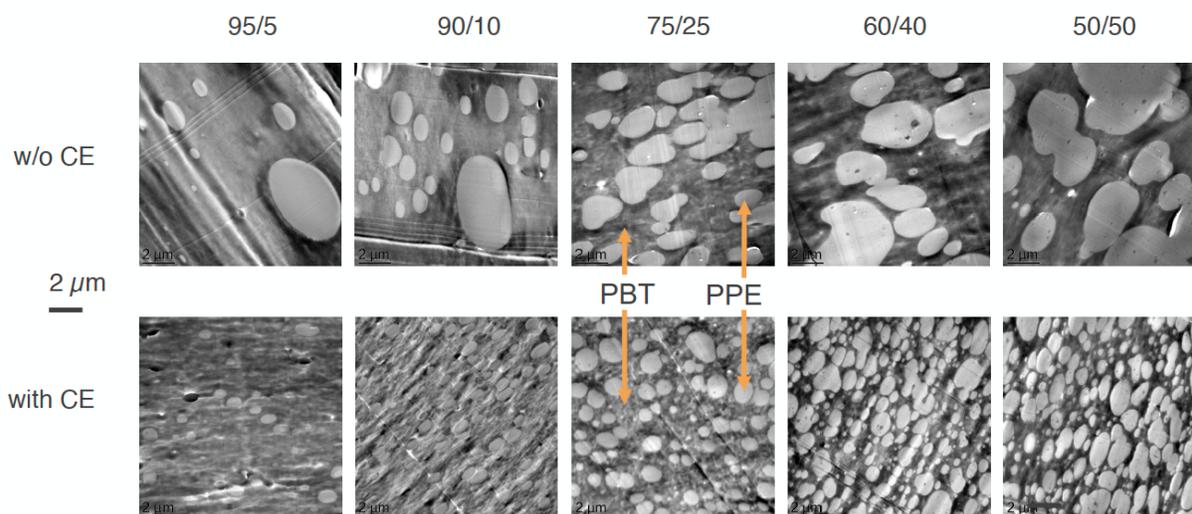


Figure 2: TEM images of the compact blends with different PBT/PPE ratios. On top: without CE. Below: with CE.

Bead Foams

Bead foams with different PPE contents were produced in a continuous extrusion process. Eminently, melt processing was more challenging when increasing the PPE content. A stable process could only be established up to a PPE content of 10 wt.-%. Above this PPE concentration, high pressure peaks were noted leading to unfavorable extreme torques which consequently caused process shutdowns. The use of 1 wt.-% CE was beneficial to enable a sufficient expansion and maintain a fine and homogeneous cell structure. An overview of the achieved foam morphologies – similar to a previous work [11], where we showed the influence of the changes of several material and processing parameters on the appearance of the beads – can be seen in Figure 3.

The chain extended PBT bead foam shows a density of 185 kg/m^3 and average cell sizes of approximately $171 \mu\text{m}$. The blend of 95 wt.-% PBT and 5 wt.-% PPE lead to non-spherical beads with higher density and irregular cell sizes. A remarkable effect on the expansion as well as on the homogeneity of the cells could be achieved when adding CE. It could be assumed that the finer dispersed PPE phase could act efficiently as nucleating points for the cells. Consequently, foamed beads with a density of 130 kg/m^3 and a cell size of $163 \mu\text{m}$ could be achieved. By adding 10 wt.-% PPE the viscosity raised and the expansion was hindered compared to the lower PPE concentration. Hence, beads with a density of 180 kg/m^3 were obtained.

The beads could be consolidated to plates by applying radiofrequency. Even though the fusion was generally possible, it has to be noted, that in this case the fusion quality was rather low resulting in brittle plates. Furthermore,

to enable good contact the beads had to be compressed within the mold, leading to increased part densities above 200 kg/m^3 .

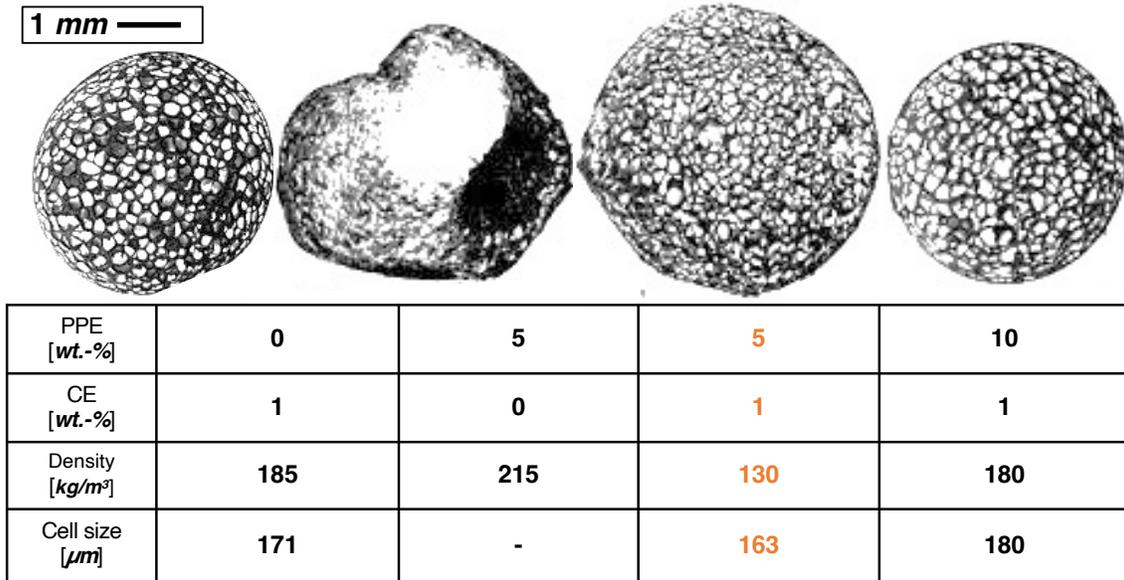


Figure 3: SEM images of the bead foams and information on density and cell sizes.

Cone Calorimetry

The results from the cone measurements are shown in Figure 4. Compared to a reference made from EPP, E-PBT burns with a higher peak heat release rate. Hence, the samples made from PBT/PPE blends burn with less energy and also show a drastic decrease in peak heat release rate (PHRR) of about 50 %. Furthermore, it is noteworthy that the total heat release (THR) and total smoke production could be reduced by the addition of PPE. Reason for the improved flame retardancy with PPE is the formation of a layer that covers the polymer surface and thereby limits the oxygen supply. While EPP and E-PBT completely burn, the blends leave a residue.

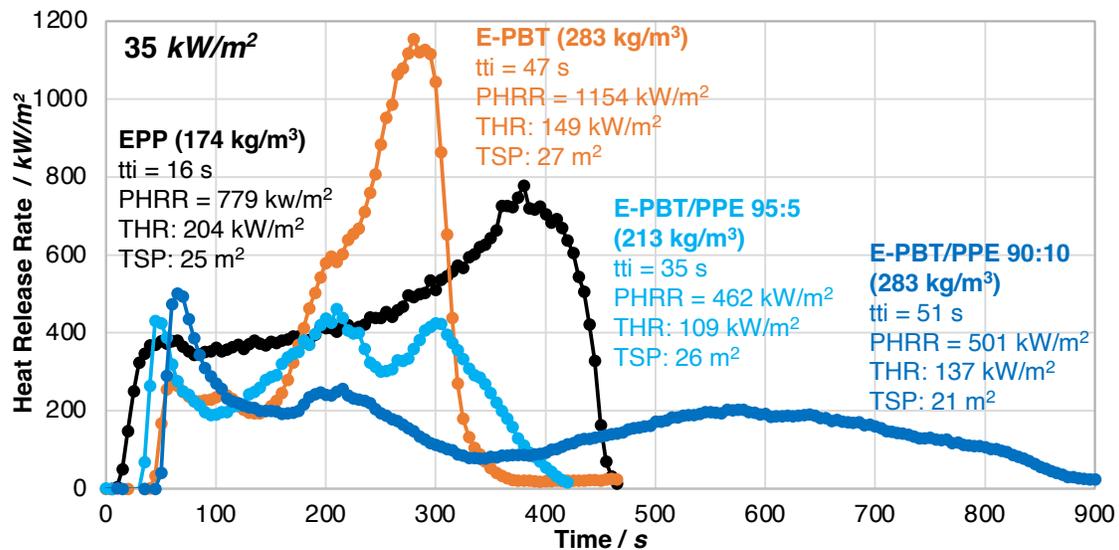


Figure 4: Results of the cone measurements for bead foams made from different PBT/PPE blend compositions and EPP as reference at 35 kW/m^2 . Values for time to ignition (tti), peak heat release rate (PHRR), total heat release (THR) and total smoke production (TSP) are given for all samples. (data partially taken from a own former work [5])

CONCLUSION

In this work PBT was blended with PPE. Here, the addition of an epoxy-based chain extender lead to a significant reduction of PPE droplet size. The chain extender itself reacts selectively with the PBT component resulting in an increase of its melt viscosity and the formation of nonlinear chains. Processing of PPE and blends with a high PPE content is challenging. Bead foams were produced in a continuous process. Here, the maximum PPE content in the blend composition that still allows a stable process was found to be 10 wt.-%. Bead foams with densities below 180 kg/m³ and a fine and homogeneous cell structure were achieved. Beads were fused using the novel radiofrequency technology. The use of the intrinsically flame-retardant PPE results in an improved burning behavior. The overall energy release and the peak heat release rate could be decreased significantly.

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