The foaming behaviour of polymer blends was systematically investigated using carbon dioxide as a blowing agent. Two batch-processing techniques were used to prepare specimens of different size. Various binary mixtures over a wide compositional range were selected as reference materials, in particular including immiscible (poly(2,6-dimethyl-1,4-phenylene ether)/poly(styrene-co-acrylonitrile) (PPE/SAN) blends. Moreover, the influence of a compatibilization with block copolymers was investigated for PPE/SAN blends. The resulting foam morphology was characterised by evaluating the density, the cell size distribution, the cell wall morphology and the compression behaviour. Besides the commonly accepted key criteria for foaming neat polymers, our study identified significant factors determining the foamability of blends such as the blend morphology, the rheological and the thermal properties. Interestingly, the compatibilization of these PPE/SAN blends by block copolymers was identified as a technique to establish micro- and submicrocellular foam morphologies with nanostructured cell walls. In view of these results, new pathways for the tailoring of cellular blends are derived.

Introduction

Over the last decades, the foaming of polymeric materials has evolved into a well-developed technology for providing cellular materials with a set of desired properties. As a result, today’s foams can cover an enormous range of applications such as load bearing, energy absorption, thermal as well as acoustic insulation. However, the demand for fine-tuned, but also novel property profiles such as controlled cell morphologies, improved barrier or mechanical properties, is steadily growing. Here, the foaming of multiphase blend systems in particular can be identified as an approach that could potentially satisfy these requirements and, thus, can be regarded as a topic of significant interest, both from the scientific as well as from the commercial point of view.

There is an extensive body of literature on regarding the foaming behaviour of polymers as well as that of filled polymers based using a variety of processing techniques [1,2]. Notwithstanding the capability to develop new classes of cellular materials by polymer blends, the literature, in particular on foamed multiphase systems, is still limited. Understanding and controlling the foaming process of blends could offer completely new possibilities with regard to fine-tuning both the processability and resulting properties as well as to developing new foam morphologies [3], as demonstrated by first approaches [4-6]. Nevertheless, the potential of polymer blends, demonstrated in numerous fields of applications [7], has not been fully exploited for foaming yet.

In this study, the batch foaming of polymer blends is systematically evaluated. Various binary mixtures of amorphous components are selected as reference materials, including immiscible poly(2,6-dimethyl-1,4-phenylene ether)/poly(styrene-co-acrylonitrile) (PPE/SAN), in particular. Furthermore, the influence of compatibilization with triblock copolymers is investigated for PPE/SAN blends.
Experimental

Polystyrene (PS, BASF, grade 145D, glass transition temperature 104 °C), polystyrene-co-acrylonitrile (SAN, BASF, VLL19, 114 °C) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE, MEP, PX100F, 216 °C) were used as received for melt-blending. Immiscible PPE/SAN and PS/SAN blends were prepared by twin-screw extrusion (Brabender, DSE 20/40) and subsequently pelletized. Moreover, PPE/SAN blends were melt-compatibilized by different contents of polystyrene-b-polybutadiene-b-poly(methyl methacrylate) triblock terpolymers (SBM, 33 wt% PS, 34 wt% PB, 33 wt% PMMA, Mn=94 kg/mol, MWD=1.02). Such a compatibilization step leads to nanostructured blend morphologies, also referred to as ‘raspberry morphology’ [8]. Further material characteristics have been discussed in detail elsewhere [8,9].

The rheological behaviour of the blends under uniaxial elongational flow was characterized by the so-called Rheotens method [10], using the compounded pellets as prepared. The experimental set-up for the Rheotens measurements includes a device for continuously providing an extruded melt strand, in the present case a high-pressure capillary rheometer (Rheograph 6000, Goettfert), combined with the Rheotens-apparatus for the uniaxial elongation of the melt. Using a tubular die (diameter 2 mm, length 30 mm) and a constant piston speed of the capillary rheometer (0.3 mm/s), the melt strand was supplied at an average die exit velocity of 10.8 mm/s (wall shear rate of 43.2 s⁻¹). The melt strand is subsequently fed to the Rheotens unit and was continuously drawn down between the two counter-rotating wheels of the device, mounted on a balanced beam. The distance between the die and the wheels was set at 96 mm. The starting velocity of the wheels was adjusted to the die exit velocity of the melt strand. The speed of the wheels was linearly accelerated at 24 mm/s² until rupture of the melt strand occurred. The force required to draw-down the melt strand was continuously measured as a function of the angular speed of the wheels. The obtained force-velocity-curves were converted into elongational viscosity-elongation rate-curves by fitting the experimental Rheotens data using a Levenberg-Marquart routine and by applying the analytical Wagner model [11].

Compression-moulding was used to prepare specimens for both the carbon dioxide solubility measurements as well as for the batch foaming experiments (20 mm x 20 mm, thickness 2 mm). Batch-foaming was performed according to the process first outlined by Suh et al. [12]. Prior to the batch foam process, the vacuum-dried specimens were saturated with carbon dioxide in a pressure vessel at a pressure of 5 MPa and a temperature of 40 °C. A minimum of 6 days was allowed to ensure uniform gas saturation. Following a fast pressure release (~ 25 bar/s), the samples were rapidly submerged in a silicon oil bath maintained at the desired foaming temperature between 140 °C and 220 °C. Foaming times were set at 10, 20, and 30 s, respectively; the foamed specimens were subsequently quenched in a water bath in order to stabilise the foam morphology. The solubility of the material was observed by evaluation of the desorption behaviour following saturation according to the method of Berens et al. [13]. In addition to this standard batch-foaming process, an advanced technique was developed to observe foamed plates with a dimension up to 400 x 200 x 50 mm³. In a gas-proof high-pressure mould, the polymer pellets were first exposed to a relatively low pressure of carbon dioxide (12 bar) at a defined gas volume of the mould. After sealing the mould, the gas pressure was subsequently increased up to approximately 30 MPa by compression. During the next step, the temperature was increased up to 180 °C under isobaric conditions and kept constant for 1 h. Such a procedure ensured homogeneous and fast ‘saturation’ of the polymer melt with a defined amount of carbon dioxide. Under isobaric conditions, the temperature was finally decreased again, well below the glass transition temperature of SAN. Following this procedure, a specimen homogeneously ‘saturated’ with carbon dioxide was observed, which could easily be foamed in a convective oven at elevated temperatures (130 °C).

Analysis of the foamed specimens included an investigation of the foam morphology as well as evaluation of the mean cell size, the cell size distribution, and the foam density. A scanning-electron-microscope (SEM) (Jeol IC 848, Leo 922), operating at an acceleration voltage of 15 kV.
and 2 kV, respectively, was used to obtain micrographs of the cellular morphology of the core region of the foamed specimens. For the microscopy, the foam samples were freeze-fractured in liquid nitrogen and the fracture surfaces were sputter-coated with gold (12 nm) or platinum (2 nm). The foam density was measured by the buoyancy method according to ISO 1183. Three specimens for each material and set of parameters were evaluated and the average value showing a standard deviation of less than 4% is reported.

The size of the polymer foams prepared by the advanced batch foaming technique further allowed to characterize the compression behaviour. Cubic specimens (17 x 17 x 17 mm3) were cut from the foamed plates and tested under uniaxial compression at 23 °C and 50 % relative humidity using a Zwick Z050 universal testing machine. A minimum number of five specimens were used for each individual material composition and the average values are reported. The compressive modulus was determined at a crosshead speed of 1 mm/min. Reaching a sample deformation for observing the modulus, the crosshead speed was increased to 5 mm/min and was kept constant until a maximum compressive stress of 8 MPa was observed.

Results and Discussion

(a) Standard batch foaming

Regardless of the processing technique applied, the foaming of polymers by using physical blowing agents, such as carbon dioxide or nitrogen, relies on the same principles: (1) saturation with the blowing agent at high pressures, (2) supersaturation of the one-phase polymer-gas mixture by reducing the pressure and/ or increasing the temperature, (3) nucleation of foam cells by the created thermodynamic instability, (4) growth of the cells, driven by the diffusion of the blowing agent, until either cell stabilisation or rupture occurs. The growth rate is primarily controlled by the diffusion rate, the rheological properties of the polymer, the gas solubility and the processing conditions. In Fig. 1, one of these factors, the solubility of carbon dioxide under the selected processing conditions, is shown. As can be seen, the solubility of immiscible PPE/SAN blends scales with the blend composition, while the difference between neat PPE and SAN is rather small. In all cases, the gas solubility is sufficiently high to allow foaming of the blend.

![Fig. 1: Solubility of carbon dioxide in PPE/SAN blends (at 50 bar and 40 °C).](image-url)

As can be seen in Fig. 2a, the elongational viscosity of immiscible PPE/SAN blends at 180 °C steadily increases up to PPE contents of 20 wt% - a behaviour similar to other particle filled systems [16]. A further increase in PPE content leads a shot-up in viscosity, associated with the onset of percolation of PPE. In order to relate the observed rheological behaviour to model systems described in literature, the zero elongational viscosity was further evaluated. For this purpose, the
ratio between the relative zero elongational viscosities of the PPE/SAN blends and of the SAN and
the so-called relative zero shear elongational viscosity, \( \eta_{rel} \), was evaluated as function of the PPE
content and was compared to the Krieger-Dougherty theory [17]:

\[
\eta_{rel} = \left(1 - \frac{\phi}{\phi_{\text{max}}}\right)^{2.5}\phi_{\text{max}}
\]

(1)

where \( \phi \) and \( \phi_{\text{max}} \) denote the volume content of a purely elastic filler and the maximum packaging
density, respectively. According to the literature, a value of 0.71 was taken to describe the
present case [18]. The good agreement between the model and the experimental values shown in
Fig. 2b reflects the hydrodynamically dominated flow occurring in PPE/SAN blends at low
elongation rates and moderate PPE contents, where PPE acts as elastic filler [18].

Similar to the rheological properties, the density of the foamed blends remains similar up to
20 wt%. Driven by the continuous development of a more continuous PPE phase, a further increase
significantly reduces the expandability and the attainable density reduction (Fig. 3a). The
 corresponding foam morphologies of SAN as well as of selected PPE/SAN blends highlight that the
presence of even small amounts of PPE significantly reduces the cell size (Fig. 3b). Simultaneously,
the cell density increases, while the density remains rather constant. Such behaviour can be
attributed to heterogeneous nucleation phenomena of the dispersed PPE phase, dominating the
homogeneous nucleation at the selected experimental conditions [19]. However, steadily increasing
the PPE content not necessarily improves the cellular structure, but also deteriorates the
homogeneity of the cells and, moreover, reduces the achievable density reduction. These effects can
be attributed to the increased viscosity, the increase in PPE phase size and the reduced strain
hardening behaviour, mainly driven by the presence of the dispersed, elastic PPE phase [16].
The compatibilization of PPE/SAN blends by SBM triblock terpolymers can be regarded as a promising strategy to overcome the otherwise poor foamability at elevated PPE contents. Following this approach leads to a reduction of the overall PPE phase size, to a reduction the glass transition temperature of PPE, to an adjustment of the viscosity behaviour as well as to an enhancement of the interfacial adhesion between PPE and SAN. The selective miscibility of the end blocks of SBM triblock terpolymers with the blend components ensures compatibilization of the system and, furthermore, the PS block, selectively entangled with PPE, reduces the high glass transition temperature of PPE [8]. As demonstrated in Fig. 4, the compatibilization step clearly affects the foam morphology of a PPE/SAN 60/40 blend by 20 wt% of SBM, when compared to the uncompatibilized blend. The homogeneity is strongly enhanced and the mean cell size is further reduced to values well below 1 µm; in the present case, the number-averaged cell size is in the range of 350 nm. Moreover, the significantly improved phase adhesion leads to an incorporation of the still more dispersed PPE phase into the cell walls and struts, and no pronounced interfacial failure can be detected. It should be noted that the solubility of carbon dioxide remains rather similar under the selected experimental condition, when compared to the PPE/SAN 60/40 blend.
reproducibility. Nevertheless, the specimens observed by such a processing technique are rather small in general which complicates further characterization steps and, as an example, strongly limits the significance of the observed mechanical properties. As a simple up-scaling of the described technique by using larger specimens for the saturation step would necessitate strongly increased saturation times (time ~ (thickness)^2), the development of new batch-foaming procedures is needed and highly demanded. In the following section, we will describe the results observed by our novel approach which allows to process rather large specimens in a reasonably short time scale.

(b) Advanced batch-foaming

For the evaluation of the foaming behaviour of blends by the advanced batch-foaming technique, the easily foamable neat SAN was selected as a starting point. Following this approach, the density of foams prepared of neat SAN is in the range of 67 g/l (Fig. 5). The stepwise addition of PPE does not significantly affect the foam density in the case of low PPE contents. However, a strong increase can already be detected at 20 wt% of PPE. Again, the reduced expandability can be attributed to the development of a more continuous PPE phase and the increased viscosity. Moreover, the effect appears to be more pronounced compared to standard batch-foaming which is likely to results of the longer foaming times (~ 20 min, compared to 10 s).

Similar to the previous studies, the influence of compatibilization was subsequently investigated. Here, the ratio between PPE and SBM was kept constant (48/20), similar to the ratio observed for a PPE/SAN/SBM 48/32/20 blend. As an example, a PPE/SBM content of 5 wt% denotes a PPE content of 3.5 wt% and an SBM content of 1.5 wt%. As can be seen in Fig. 5, the compatibilization by SBM allows to obtain low density foams over a wide range of compositions; only at 40 wt% of PPE/SBM, a remarkable increase can be detected, leading to a identical density as observed for SAN blends with 20 wt% of PPE. Similar effects previously described for the other batch-foaming technique are likely to be responsible for such a behaviour, e.g. a reduced phase size of PPE as well as an enhanced interfacial adhesion between PPE and SAN. Finally, the influence of adding a low viscous blend phase, polystyrene (PS), was investigated. As can be seen, the foam density remains rather constant within the selected range of compositions (max. 20 wt% of PS). For all foamed blends, heterogeneous nucleation activity led to a significant reduction of the cell size (tens of micrometers) when compared to neat SAN (hundreds of micrometers). In all cases, the cell size was remarkably higher for foams prepared by the advanced batch-foaming approach, in comparison to the standard technique. A more detailed investigation of the cell size distribution is beyond the scope of the present study, but will soon be published elsewhere.

Fig. 5: Foam density of SAN-based blends using the advanced batch-foaming technique (foaming temperature 130 °C).
The compression behaviour of selected foamed blend materials is shown in Fig. 6. As can be seen, a similar behaviour can be detected for neat SAN and SAN blends with either 20 wt% of PPE/SBM or 10 wt% of PPE, respectively, which can be attributed to the similar foam density. At elevated contents of PPE (20 wt%) or PPE/SBM (40 wt%), both the compressive modulus and the compressive strength remarkably increase which is driven by the higher foam density. It is worth to be mentioned that both foam materials show a slightly distinct behaviour at elevated levels of compressive strain which may be effected by the different micromechanical response of the blend material [20].

![Fig. 6: Representative stress-strain curves under compression of selected SAN-based foams, processed by the advanced batch-foaming technique (foaming temperature 130 °C).](image)

In order to more precisely evaluate the mechanical property profile of the foamed blend materials, the compressive strength and the compressive modulus are shown as a function of foam density in Fig. 7. As can be seen, the mechanical response is primarily controlled by the foam density. Comparing the neat SAN foams with the foamed blends, a slight enhancement can be detected, in particular for the modulus behaviour. The reduced cell size of the foamed blends is likely to induce this improvement. Moreover, at elevated foam densities, inhomogeneous foam morphologies may lead to the degradation of the strength behaviour, as premature failure is induced by macroscopic foam defects. More detailed investigations, e.g. correlating the foam morphology to the mechanical behaviour, will be presented in our next publication.

![Fig. 7: Compression behaviour of the foamed SAN-based blends as a function of density, processed by the advanced batch-foaming technique (foaming temperature 130 °C). (a) Compressive strength. (b) Compressive modulus.](image)
As the modulus and the strength behaviour of the foams can only slightly be enhanced via the blending approach, the question of further properties arises which can beneficially be improved. Besides the limited enhancement of the mechanical properties, the improvement of the barrier properties appears as a rather promising candidate. In order to reduce the permeability to a certain gas or liquid, a highly non-permeable, but dispersed blend phase needs to be incorporated into the cell walls as a highly elongated component [7]. In the present case of SAN-based blends, this requirement is fulfilled only for blends of SAN with a lower viscous PS phase (Fig. 8, left picture). In contrast, the high-viscous PPE phase does not elongate in the field of extensional flow, but acts as dispersed, spherical, solid-state filler. It can thus be concluded that the successful exploitation of foamed polymer blends as barrier materials requires adjusted rheological properties which allow to control the cell wall morphology [21].

![Fig. 8: Morphology of the cell walls of PS/SAN 10/90 (left) and PPE/SAN 10/90 blends (right), processed by the advanced batch-foaming technique (foaming temperature 130 °C).](image)

Conclusions

This detailed investigation identified additional factors determining the foamability of multiphase blends, besides the commonly accepted key criteria of neat polymers including sufficient gas solubility and diffusion rates, suitable processing conditions and balanced rheological properties. In the case of multiphase blends, the significant influence of the initial blend morphology, of the rheological as well as of the thermal properties of the respective phases and the blend needs to be taken into account. Furthermore, the compatibilization of these PPE/SAN blends by block copolymers could be identified as a technique to establish micro- and nanocellular foam morphologies with nanostructured cell walls.

The refined foam morphology allows to enhancing the mechanical properties of foamed blends when compared to neat polymers. However, the exploitation of the blending approach appears even more promising to establish cellular barrier materials. Here, the rheological properties of the blend phases need to be carefully adjusted to control the morphology development in the cell walls. As demonstrated by using advanced batch-foaming techniques, higher viscous, dispersed blend phases in SAN, such as PPE, are detrimental to observe barrier materials; in contrast, lower viscous phases such as PS can be highly elongated in the field of elongational flow occurring during cell growth and, as a result, can potentially act as a barrier.

In view of these results on selected blend systems, additional criteria determining the foamability of polymer blends as well as the morphology of the cell walls can be determined and, furthermore, new pathways for the controlled tailoring of cellular blends are derived.

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