Recycled PET foaming: Supercritical carbon dioxide assisted extrusion with real-time quality monitoring

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ABSTRACT

Foaming of recycled poly(ethylene terephthalate) (rPET) was performed by supercritical carbon dioxide (sc-CO2) assisted extrusion. The intrinsic viscosity (IV) of rPET was increased from 0.62 dl/g to 0.87 dl/g using an epoxy-functional chain extender, which provided adequate rheological properties for cell stabilization so that an apparent density of less than 0.15 g/cm3 became achievable. Homogeneous and talc induced heterogeneous crystal and cell nucleation, subsequent cell growth and stabilization processes were examined using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. It was found that using talc the crystallization temperature increases which results in smaller cell size distribution. A strong correlation was evinced between the apparent density and the Fourier transform near-infrared (NIR) spectrum of the foamed rPET samples enabling quick and non-destructive characterization. Accordingly, NIR spectroscopy is demonstrated as a suitable method for in-line quality monitoring during extrusion foaming of recycled PET, being especially prone to quality fluctuations.

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1. Introduction

Industrial development poses a number of new challenges for plastic processing. Important tasks are to continuously ensure the quality of the products, to develop the flexibility of the production processes, and to increase the efficiency of production. In addition to the introduction of Industry 4.0, for sustainable development, the aspects of the circular economy must also be taken into account, in which the high-level recycling of used plastic products is an important pillar [1]. The recent crisis caused by the coronavirus (SARS-CoV-2) has led to the closure of many community meeting and dining venues, resulting in increased consumption of retail food and more frequent home delivery, and thereby a rapid rise in single-use plastic packaging and their waste [2]. In the case of thermoplastic polymers, recycling can be efficiently realized physically by melt processing after the collection and purification of the selectively collected or separated discarded products [3].

Poly(ethylene terephthalate) (PET) is one of the most commonly used thermoplastics in the world, an annual volume of 19 million tons is produced for short-lived packaging [4]. These typical bottle products usually appear in the waste stream even in the year of manufacture [5], or in the worst case due to irresponsible human behaviour in the environment [6], causing significant environmental impact [7]. After proper collection, sorting, washing, and purification, recycling is possible, but this process is hampered by the degradation of the molecular chains. In addition to UV radiation on products [8,9], hydrolytic and thermal degradation during processing are primarily responsible for the shortening of the molecular chains [10,11]. Degradation reduces the melt viscosity of the
material [12–14], which can cause processing difficulties. The aesthetic and functional mechanical properties of the produced secondary raw material or products are also negatively affected by degradation [15,16]. In the case of PET, the average length of the molecular chains is generally characterized by the intrinsic viscosity value determined by solution viscosity [17]. The intrinsic viscosity value of the original raw material used for bottle production is usually in the range of 0.78–0.82 dl/g [18], but during processing this value can also decrease by 0.06–0.08 dl/g.

Involving foaming in the recycling process can provide an opportunity to produce new, even longer-lasting products that can be used for heat and sound insulation purposes, e.g. in the field of construction. In this field, it is advantageous that thermoplastic PET foam products can be physically recycled after use, as opposed to crosslinked foams (e.g. polyurethane). This application area requires the production of suitably low-density, uniform-quality, homogeneous foams by a productive process. Low density can be achieved primarily with physical blowing agents (PBAs) (e.g. N2 or CO2 gas or supercritical fluid), the appropriate cell density and cell size distribution are mainly from nucleating agents (e.g. include calcium carbonate, calcium stearate, magnesium silicate, the mixture of citric acid and sodium bicarbonate, rubber particles, sodium benzolate, stearic acid, silica products, talc, and zinc stearate), technological parameters (temperature, pressure) and characteristics of the polymer (e.g. molecular weight, branching) [19,20]. External particles or surfaces work as heterogeneous nucleating sites during foaming [21]. The heterogeneous nucleation decreases the energy-barrier dramatically for cell nucleation, increases the nucleation rate, and is expected to narrow the cell size distribution [22]. Productivity is best provided by extrusion foaming, which has significantly higher yields than batch foaming, compression moulding, or even injection moulding.

Extrusion foaming with supercritical CO2 (sc-CO2) enables the manufacturing of products with very light (\( \rho = 3–50 \text{ kg/m}^3 \)) apparent density \[23,24\]. The purposeful process consists of three parts: in the first step, liquid CO2 is introduced into the polymer melt under high pressure, where rapid mixing and dissolution of the in–situ formed supercritical sc-CO2 in the polymer melt occur. This step takes place in the extruder, where a saturation concentration is reached under the given conditions. In addition to temperature and pressure conditions, saturation is also affected by gas solubility and residence time. In the second step, the polymer/gas solution exits the die, during which there is a sudden pressure drop, which drastically reduces the solubility of the gas and results in phase separation. This is the cell nucleation step that determines the resulting cell density. The third step is cell growth, which lasts until it is hindered by opposing forces resulting from the viscosity of the matrix. The resulting cell size is determined by the cooling and pressure conditions, the concentration of gas dissolved in the melt, and the viscoelastic properties of the matrix [25]. If the viscosity of the matrix is inadequate, the cells may coalesce and/or collapse during growth, which significantly impair the resulting density [26].

Foaming of recycled PET has been the focus of research since the mid-1990s due to the increasing amount of waste generated and the new advances in molecular weight increasing processes. The quality of the raw materials used in the research, the technology used, and the average cell size achieved, as well as the apparent density, are summarized in Table 1. It can be stated that a lower apparent density can be achieved with physical foaming than with chemical foaming, which can be mainly explained by the higher cell density characterizing the nucleation behaviour. It can also be observed that with the batch technology of the physical processes, a density of less than 0.1 g/cm³ is achievable, which can be explained by the significantly longer diffusion time compared to extrusion technology.

The viscoelastic properties of the polymer melt play an important role in the resulting cell distribution of the foam product. Several have shown that methods that create chain branches significantly increase melt elasticity and increase relaxation time compared to linear chain lengthening, which also helps prevent cell fusion, thereby making cell growth more stable [26–30].

Methods that are commonly used for the qualification and quality control of the structure of foams are either batch procedures, performed with samples taken from production, or in-line applicable during continuous production. The advantage of in-line measurements is that the quality of the foamed products can be monitored in real time and preferably in a non-destructive way. If there is a change in the tested characteristic, it is possible to immediately change the production parameters (e.g. zone temperature, pressure, screw speed, CO2 flow rate) through signal processing and feedback, so that in-line control can be established. An in-line FT-NIR measurement system for co-extrusion foaming technology was developed by Nagata et al. and successfully used to determine the CO2 concentration in the polymer [31,32]. Tatibouet et al. used an in-line ultrasonic technique, built into the extruder to determine the onset of phase separation in the polymer melt [33,34]. Common et al. used Raman spectroscopy to characterize residence time and mixing during extrusion foaming [35].

The aim of the present research was to develop recycled PET raw materials using chain extender and nucleating additives that can be used to produce low-density (microcellular) foams. Based on literary antecedents (Table 1), by processing PET recylcates with typical intrinsic viscosity values of 0.70–0.90 dl/g using the industrially more relevant extrusion foaming technology, the achievable foam density is limited to the range of 0.8–0.9 g/cm³. An expection is our previous study, where foams with density of 0.24 g/cm³ were produced by sc-CO2 assisted extrusion using PET bottle regrinds with an intrinsic viscosity of 0.74 dl/g as starting material [29]. In this work, our extrusion technology has been further developed, and not only to achieve lower apparent densities, but to create and validate an in-line applicable non-destructive measurement procedure for continuous quality (density) control of the recycled foams, being especially prone to quality fluctuations.

2. Materials and methods

2.1. Materials

PET bottle flakles (Jász-Plasztik Ltd., Hungary), originating from collected, washed, and sorted post-consumer PET bottles, with an intrinsic viscosity value of 0.73 dl/g were used as matrix material. As nucleating agent, HTPaltr5L type talc (IMI FABI SpA, Italy), with a median particle diameter of 0.65 μm was used. To increase melt viscosity and intrinsic viscosity, a styrene-acrylic oligomer multifunctional epoxide chain extender, Joncryl ADR 4468 (BASF SE, Germany) with a molecular weight of 7250 g/mol and an epoxy equivalent weight of 310 g/mol [50,51] (specific gravity: 1.08 g/cm³; glass transition temperature: 54 °C) was used.

2.2. Methods

The rPET flake were dried for 4 h at 160 °C, before compounding, LTE 26–44 (Labtech Engineering, Thailand) twin-screw extruder was used for the mixing with zone temperatures between 245 and 260 °C.

Intrinsic viscosity value was used for characterisation of the average molecular weight. The relation between the intrinsic
sc-CO$_2$ assisted extrusion foaming was carried out on a modified injection moulding to measure the complex shear viscosity over a frequency sweep tests were performed at 260 °C. Two parallel-plate geometry. Dynamic AR 2000 type rotational rheometer (TA Instruments, New Castle, DE, USA) with 25 mm diameter parallel-plate rheometer equipped with an optical sensor. Phenol-tetrachloroethane mixture in the ratio of 60:40% was applied as a solvent, concentration was 0.5 g/dl, and examination temperature was 30 °C. Two parallel-plate measurements were performed in all cases. Melt rheology under dynamical shear was investigated using an AR 2000 type rotational rheometer (TA Instruments, New Castle, DE, USA) with 25 mm diameter parallel-plate geometry. Dynamic frequency sweep tests were performed at 260 °C in nitrogen atmosphere to measure the complex shear viscosity over a frequency range of 0.1–100 Hz. Prior to foaming, the regranulates were dried at 160 °C for 4 h. Sc-CO$_2$ assisted extrusion foaming was carried out on a modified Collin Teach-Line ZK 25T type co-rotating twin-screw extruder (Dr Collin GmbH, Ebersberg, Germany) with a screw diameter of 25 mm and an L/D ratio of 24. The extruder has 5 heating zones: 1–3, zone plasticizing and melt transport section; the sc-CO$_2$ is introduced into the 4, zone using a syringe pump (Teledyne Isco 260D, Lincoln, NE, USA). This is followed by the last (zone 5) of the extruder, followed by the melt pump and the static mixer, which ensure even, homogeneous mixing and material flow. The temperature of these elements and the pressure drop across them were continuously monitored. The die had a circular cross-section with an opening of 2 mm in diameter. The continuously exiting foamed products were collected using a conveyor and cooled in the air. NIR spectra were collected using a Bruker Optics MPA™ FT-NIR spectrophotograph (Bruker Optik GmbH, Ettlingen, Germany) equipped with a Solvias fiber optic probe (Solvias AG, Kaiseraugst, Switzerland) in reflection mode. The instrument was set to provide a spectral range of 4000–12500 cm$^{-1}$ with an 8 cm$^{-1}$ resolution. For model building, three NIR spectra were collected with 10 kHz scan speed and by averaging 32 scans from different locations of 36 samples, differing in apparent density, of both types of PET foams. The same settings were used for in-line sampling, except the in-line spectra were calculated from 16 scans to reduce sampling time. SEM micrographs were obtained using EVO MA 10 instrument (Zeiss, Germany) at an accelerating voltage of 30 kV on specimens coated by 32 nm gold layer. The mean value and standard deviation of the diameter of the cell cross-sections approximated by a circle were determined from 250 to 400 measurements per sample. Void fraction or porosity is defined as a fraction of the volume of voids over the total volume as a percentage. To determine the apparent density, porosity and expansion ratio of the foams, density measurements were performed by immersion method according to ASTM D792-13. Void fraction or porosity is defined as a fraction of the volume of voids over the total volume as a percentage. The percentage of void fraction ($V_f$) was calculated from apparent density ($\rho_{app}$) of foams and the density of the non-foamed extrudate ($\rho$) according to Equation (2):

$$V_f = 100% \times \left[ 1 - \left( \frac{\rho_{app}}{\rho} \right) \right]$$  \hspace{1cm} (2)

Density ($\rho$) of the non-foamed PET based polymer mixtures were considered to be 1.375 g/cm$^3$ (without talc) and 1.383 g/cm$^3$ (with talc), while $\rho_{app}$ of expanded samples was measured by Radwag AS 60/220.R2 analytical balance with density measurement kit in ethanol. The expansion ratio ($\Phi$) was calculated according to Equation (3):

$$\Phi = \frac{\rho}{\rho_{app}}$$

<table>
<thead>
<tr>
<th>Initial intrinsic viscosity [dl/g]</th>
<th>Chain extender additive or process</th>
<th>Modified intrinsic viscosity [dl/g]</th>
<th>Foaming technology</th>
<th>Type of foaming agent</th>
<th>Apparent density [g/cm$^3$]</th>
<th>Average cell diameter [µm]</th>
<th>Cell density [cells/cm$^3$]</th>
<th>Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>–</td>
<td>–</td>
<td>batch</td>
<td>PBA</td>
<td>no data</td>
<td>2</td>
<td>4.4×10$^{11}$</td>
<td>1995</td>
<td>Baldwin et al. [36]</td>
</tr>
<tr>
<td>0.78</td>
<td>tetrafunctional epoxy</td>
<td>no data</td>
<td>batch</td>
<td>PBA</td>
<td>0.80 65</td>
<td>no data</td>
<td>1998</td>
<td>Xanthos et al. [27]</td>
<td></td>
</tr>
<tr>
<td>0.74</td>
<td>PMDA</td>
<td>0.95</td>
<td>extrusion</td>
<td>PBA</td>
<td>0.20 270</td>
<td>no data</td>
<td>2000</td>
<td>Japon et al. [37]</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>–</td>
<td>–</td>
<td>compression moulding</td>
<td>CBA</td>
<td>0.82 52</td>
<td>8×10$^{6}$</td>
<td>2004</td>
<td>Guan et al. [39]</td>
<td></td>
</tr>
<tr>
<td>0.49</td>
<td>PMDA</td>
<td>0.77</td>
<td>extrusion</td>
<td>CBA</td>
<td>1.17 50</td>
<td>1.2×10$^{6}$</td>
<td>2005</td>
<td>Maio et al. [40]</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>–</td>
<td>–</td>
<td>batch</td>
<td>PBA</td>
<td>0.06 25</td>
<td>10$^{3}$</td>
<td>2010</td>
<td>Sorrentino et al. [42]</td>
<td></td>
</tr>
<tr>
<td>0.74</td>
<td>PMDA</td>
<td>0.88</td>
<td>batch</td>
<td>PBA</td>
<td>0.03 30</td>
<td>1.5×10$^{6}$</td>
<td>2014</td>
<td>Xia et al. [43]</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>tetrafunctional epoxy</td>
<td>no data</td>
<td>bath</td>
<td>PBA</td>
<td>0.07 86</td>
<td>no data</td>
<td>2014</td>
<td>Liu et al. [44]</td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>multifunctional epoxide</td>
<td>1.14</td>
<td>batch</td>
<td>PBA</td>
<td>0.09 30</td>
<td>5.4×10$^{10}$</td>
<td>2015</td>
<td>Yan et al. [28]</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>modified polymerization by</td>
<td>1.5</td>
<td>extrusion</td>
<td>PBA</td>
<td>0.14 265</td>
<td>4.0×10$^{5}$</td>
<td>2016</td>
<td>Fan et al. [30]</td>
<td></td>
</tr>
<tr>
<td>0.65</td>
<td>–</td>
<td>–</td>
<td>injection moulding</td>
<td>CBA</td>
<td>1.16 95</td>
<td>no data</td>
<td>2017</td>
<td>Ronkay et al. [45]</td>
<td></td>
</tr>
<tr>
<td>0.76</td>
<td>PBT-glycidyl methacrylate-</td>
<td>0.95</td>
<td>batch</td>
<td>CBA</td>
<td>no data 61</td>
<td>1.8×10$^{8}$</td>
<td>2017</td>
<td>Li et al. [46]</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>multifunctional epoxide</td>
<td>no data</td>
<td>injection moulding</td>
<td>CBA</td>
<td>1.17 100</td>
<td>no data</td>
<td>2019</td>
<td>Szabó and Dogossy [47]</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>multifunctional epoxide</td>
<td>0.96</td>
<td>extrusion</td>
<td>CBA</td>
<td>0.88 148</td>
<td>no data</td>
<td>2019</td>
<td>Lai et al. [48]</td>
<td></td>
</tr>
<tr>
<td>0.71</td>
<td>multifunctional epoxide</td>
<td>0.74</td>
<td>extrusion</td>
<td>PBA</td>
<td>0.24 219</td>
<td>no data</td>
<td>2019</td>
<td>Boczi et al. [29]</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>PBA</td>
<td>0.20 400</td>
<td>8×10$^{4}$</td>
<td>2020</td>
<td>Yao et al. [49]</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Summary of recent result in the field of PET and recycled PET foaming (PBA: physical blowing agent, CBA: chemical blowing agent).
The molecular weight of rPET was increased by reactive extrusion using 0.0 – 0.7% chain extender. The intrinsic viscosity value of the manufactured regranulates as a function of the chain extender content is shown in Fig. 1. It can be seen that without chain extender addition, the intrinsic viscosity value of rPET reduces to 0.62 dl/g due to the degradation during reprocessing by extrusion. To reach the initial intrinsic viscosity value of 0.73 dl/g approximately 0.5% chain extender is required. By using 0.7% chain extender, the intrinsic viscosity value of rPET increased to 0.87 dl/g, which value is still lower than the raw materials used for chain extender, the intrinsic viscosity value of rPET increased to approximately 0.5% chain extender is required. By using 0.7% chain extender addition (rPET + 0.7% CE) and other also chain-extended with 0.7% additive but containing 1% talc as nucleating agent as well (rPET + 0.7% CE + 1% talc).

The viscosity curves of unmodified rPET and rPET modified with 0.7% chain extender with and without talc addition, as measured at 260 °C, are shown in Fig. 2. It can be seen that the viscosity curve of materials containing 0.7% chain extender shows a different character compared to unmodified rPET, which has a wide Newtonian plateau at low frequencies and is characterized by a slight shear thinning, suggesting a linear molecular structure. Materials containing chain extender, on the other hand, show noticeably increasing viscosity and pronounced shear thinning in the low frequency range as a result of the broader molar mass distribution and the introduced long-chain branches [53]. This behaviour is favourable during foaming to stabilize the cells. Talc was found to have little effect on the nature of the viscosity curve.

The additives used to improve foamability were expected to modify the crystallization behaviour of rPET and by this means to affect the process of cell wall solidification during foaming. The crystallization characteristics characterizing the solidification of the materials used were compared by non-isothermal crystallization at different cooling rates. It can be seen in Fig. 3 that the crystallization temperature of the chain extender containing material. Crystallization temperatures even higher than those of the unmodified rPET were measured in the entire cooling rate range tested. It was concluded that talc effectively acts as a crystal nucleating agent, and by hindering supercooling, it may facilitate faster solidification of the cell walls during cooling, which is of key importance regarding stabilization of the cellular structure.

### 3. Results and discussion

#### 3.1. Improving the foamability of rPET

The crystal nucleating agent, and by hindering supercooling, it may facilitate faster solidification of the cell walls during cooling, which is of key importance regarding stabilization of the cellular structure.

#### 3.2. Foam extrusion and characterisation

At the beginning of the foam extrusion process, sc-CO2 with a constant volumetric rate of 0.5 mL/min was introduced into the barrel and mixed with the 260 °C melt. Then the resulting foam structure was stabilized by continuously lowering the melt temperature until the exiting product became highly expanded and uniform. The weight percentage of sc-CO2 within the melt was measured to be 3.5 wt%, the plasticization effect of which was significant, since even if the material temperature was below 235 °C in the mold, the material still remained in molten state. The technological parameters characterizing the
continuous production of highly expanded foams are shown in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder temp. zones [°C]</td>
<td>230–260</td>
</tr>
<tr>
<td>Screw speed [rpm]</td>
<td>25</td>
</tr>
<tr>
<td>Melt pump speed [rpm]</td>
<td>15</td>
</tr>
<tr>
<td>Melt pump temp. [°C]</td>
<td>240–245</td>
</tr>
<tr>
<td>Pressure before the melt pump [bar]</td>
<td>110–115</td>
</tr>
<tr>
<td>Temperature of static mixer [°C]</td>
<td>230–235</td>
</tr>
<tr>
<td>Temperature of die [°C]</td>
<td>230–235</td>
</tr>
<tr>
<td>sc-CO₂ rate [mL/min %]</td>
<td>0.5</td>
</tr>
<tr>
<td>sc-CO₂ pressure [bar]</td>
<td>80–85</td>
</tr>
</tbody>
</table>

Fig. 3. Crystallisation temperature vs. cooling rate based on the non-isothermal crystallisation measurements (CE: Chain extender).

Fig. 4. Photographs taken from a) unfoamed rPET; b) rPET + 0.7% CE foam; c) rPET + 0.7% CE + 1% talc foam (CE: Chain extender).

During the setting of the production parameters of highly expanded rPET foams, samples of different apparent densities were taken, the NIR spectrum of which was acquired off-line as an average of 3-3 measurement points using 32 scans. Prior to the chemometric evaluation, all spectra were normalized, smoothed, and the 1st derived spectra were evaluated in order to eliminate the intensity deviation between the measured points. The apparent density was estimated by partial least square (PLS) modelling using density measurement according to ASTM D792-13 as a reference method. The presence of talc affects the models, therefore different models were built for the samples containing and not containing talc. The number of Latent Variables (LVs) used in the models was optimized according to the R² values for calibration and cross-validation, and 3 LVs were selected for each models. The noticeable differences in the peak intensities and ratios provide a good basis for estimating the apparent density based on the NIR signal. As it can be seen in Fig. 7, there is a fairly good correlation between the density values estimated from the fitted model and the measured apparent density values for both talc-free and talc-containing rPET foam samples indicating the reliability of both models to be used for non-destructive density estimation. Somewhat higher correlation coefficient (R² = 0.911) was determined for the foams containing talc as nucleating agent, which is proposed to be attributed with the relatively constant, narrow ranges of cell density and average cell size (Fig. 6 a and b) of the analysed samples, and that no major structural change is observed in the examined range of apparent density (0.14–0.95 g/cm³). The shell layer with differing
Fig. 5. SEM images of rPET foam samples with different densities; left: with talc and right: without talc (CE: Chain extender).
thickness and structure basically influence the penetration and scattering of NIR radiation, and therefore believed to be largely responsible for the detected error between the estimated and measured density values.

The applicability of NIR signal based in-line quality monitoring of rPET foaming is demonstrated by an experiment, where the density of the extrudate with 0.7% chain extender and 1% talc content was real-time analysed by multivariate data evaluation (PLS modelling) of the continuously recorded NIR spectra. For in-line monitoring, the measurement time was reduced by calculating the spectra from 16 scans instead of the 32 scans used for model building, therefore achieving spectra acquisition every 9 s. The setup used for in-line quality monitoring of foam extrusion is presented schematically in Fig. 8.

The density values estimated during the in-line NIR sampling of the extrudates and their moving average are shown in Fig. 9. Steady state production was disrupted 180 s after the NIR sensor was turned on by increasing the tool temperature, and in parallel, the structure and density of the produced foam also changed. The test section was sampled at 5 time points for validation purposes. The actual density values, obtained by immersion method (performed according to ASTM D792-13), are also indicated in Fig. 9. It can be stated that the density values estimated by PLS modelling of the NIR spectra continuously recorded from the extrudate show a good match with the validating apparent density values,

Fig. 6. Average cell diameter (a) and cell density (b) as a function of apparent density (CE: Chain extender).

Fig. 7. Correlation between the measured and NIR signal based estimated density values (CE: Chain extender).

Fig. 8. Schematic drawing of foam extrusion with in-line quality monitoring system (1: extruder; 2: compressed CO₂ gas; 3: pump; 4: conveyor; 5: NIR sensor; 6: rPET foam; 7: data processing unit).
Therefore the method is assessed to be suitable for real-time quality monitoring of rPET foaming.

This is of great importance for industrial applicability, as the information obtained on the product’s density can provide an opportunity for immediate intervention or regulation, thus providing an opportunity for a high level of quality assurance of the manufactured recycled foam product.

4. Conclusions

During our research, it was found that reactive extrusion of bottle grade PET regrind as starting material with 0.7% chain-extending additive can produce a raw material suitable for extrusion foaming. The intrinsic viscosity value of 0.86 dl/g proved to be adequate for stable and continuous production of highly expanded foams with apparent density lower than 0.15 g/cm³.

It is presented that 1% addition of talc has a noticeable effect on both foam cell nucleation and PET crystallization. Heterogeneous nucleation increases cell induction, while crystallization at higher temperatures helps to stabilize small cells during cooling. As a result, the cellular structure of talc-containing foams become more uniform over a wide density range than that of the talc-free material. The proposed composition of starting material suitable for extrusion foaming requires minimal (less than <2%) additives, therefore it provides a cost-effective solution for the production of high-quality products even for industrial-scale implementation of recycling.

Utilizing the strong correlation evinced between the NIR spectrum and the apparent density of the rPET foams, the innovation of NIR spectrum based real-time quality monitoring is demonstrated. The proposed novel non-destructive, in-line applicable process contributes to the minimisation of production losses (wastrel) and is less time and human resource consuming than the commonly used procedures, and thus it can provide further cost savings. Similar spectroscopy-based quality control procedures are expected to gain application also in other fields where the constant physical or chemical structure of the products are important.

Declaration of competing interest

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References
