# Preparation of low-density microcellular foams from recycled PET modified by solid state polymerization and chain extension

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## ABSTRACT

*Recycled polyethylene-terephthalate (RPET) bottle regrinds were physically foamed after two types of industrially feasible molecular weight increasing processes. Intrinsic viscosity (IV) of initial waste (0.71 dl/g) increased both after reactive extrusion carried out using a multifunctional epoxy-based chain extender (0.74 dl/g) and after solid state polycondensation (SSP) (0.78 dl/g), while capillary rheometry revealed higher degree of branching in the chain extended PET material. Despite the relatively low IV values (below 0.80 dl/g), physical foaming, a mild and cost efficient way, was successful in both cases, uniform microcellular foam structures with void fractions ranging between 75 and 83% were achieved. During the experiments morphology change in the materials was tracked by differential scanning calorimetry (DSC) besides recording IV values. The IV drop during foaming was between 0.03-0.10 depending on the pre-processing technology. Structure of*

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*foams produced from the two different modified RPET materials was compared with each other based on scanning electron microscopic imaging (SEM) of cryogenic fracture surfaces. The average cell diameters were measured to be 213 and 360 µm in the case of chain extended and SSP-modified materials, respectively.*

**Keywords:** recycling; PET; physical foaming; chain extension, solid state polycondensation

## 1 Introduction

Polyethylene-terephthalate (PET) has become one of the most important plastics in the last decades. It is widespread due to its mechanical properties and high barrier ability [1]. PET is primarily used in the production of fibers and packaging materials, however is also applied as engineering plastic [2]. Since the life cycle of packaging industrial products is short the amount of PET waste increases every year [3][4]. The need for recycling increases since PET is not biologically degradable and only expensive methods exist for its degradation. On the other hand, industry also needs secondary base materials that can be produced in a cost-effective way. For this purpose, selective waste collection and high level of separation are essential requirements [5][6]. Therefore, important aim of the industry is not only to achieve adequate level in reprocessing of PET waste but also to realize value addition. A novel solution for value addition is the production of decreased density polymer foams, which can find application in packaging, energy sector and construction industry [7][8].

In case of polymer foams base material has to have high melt strength that prevents the foam from collapsing during stabilization of cell formation. Viscosity determines the polymer’s melt strength that depends on three important molecule characteristics: average molecular weight, molecular weight distribution and degree of polymer chain entanglement [9][10]. Most commercially available PET types have low molecular weight and narrow molecular weight distribution and therefore melt strength is low at foaming temperature resulting in cell collapse [9]. Production of adequate foams is even more challenging if the base material is a small molecular weight recycled PET (RPET) [11][12].

Rheological modifications are necessary to improve the foamability of RPET. For this purpose, two methods are used: the application of different chain extender additives and the solid state polymerization (SSP) [13]. The principle of chain extension method is that hydroxyl and/or carboxyl chain ends of PET oligomers are “bound” with di- and polyfunctional reagents and this way an increase in the average molecular weight, chain entanglement degree and formation of cross-bonds can be achieved [14][15][16][17]. Xiao et al. [18] applied multifunctional epoxy chain extender to increase the molecular weight of recycled PET regrinds. They found that even a small concentration (0.5 %) of the additive modifies the structure of linear PET and creates long chain branching in it. In contrast to the previous melt-method, SSP, condensation reactions take place above glass transition temperature ($T_g$) but below melting temperature ($T_m$), which can be enhanced if the system is held under vacuum and the volatile components leave continuously [19]. SSP process has been successfully applied to increase the molecular weight of recycled PET [20][21].

Polymer foaming agents can be classified according their chemical (CBA: Chemical Blowing Agent) or physical (PBA: Physical Blowing Agent) activity. CBAs degrade – initiated mainly by heat – during processing when gas that foams the polymer evolves, while in the latter case a material that is gas at normal atmosphere is injected directly. The, application of CBAs is considered, in general, resulting in a better quality cell structure (e.g. better mechanical stability etc.) since it is easier to disperse this way the foaming gas more evenly and thus achieve more homogenous and stabile cell structure. However, from environmental point of view the application of CBAs is not advantageous and their use is limited in foams applied in food packaging. In contrast, advantage of PBAs is that there is no remaining material after foaming. Furthermore, with PBAs higher expansion rates are achievable and their application is more favorable from economic aspects as well.

The use of $CO_2$ as PBA provides several advantages as it is non-flammable, non-toxic, cheap, easily achieves supercritical state and has relatively high solubility in polymers (diffusion coefficient in case of PET at 200°C is 2.6 x $10^{-6}$ $cm^2/s$ according to [22]. Dissolution of $CO_2$ in common polymers is better than that of $N_2$ [23]. The cell structure can be influenced with the volume flow rate of $CO_2$ as cell size and cell density depend on saturation pressure and quantity of the dissolved gas significantly [24].

Xia et al. [24] carried out pyromellitic dianhydride (PMDA) based reactive extrusion followed by foaming with supercritical $CO_2$ ($scCO_2$). The intrinsic viscosity (IV) value of the initial PET material (0.67 dl/g) was raised to 1.4 dl/g, and after foaming this high molecular weight material, using an autoclave based technology, expansion rates of 10-50 with characteristic cell diameters of 15-37 μm were reached.

Liu et al. [25] foamed PET with an initial IV value of 0.8 dl/g using autoclave batching foaming method and applied tetraglycidyl diamino diphenyl methane (TGDDM) as chain extender. The obtained foams had less than 0.07 $g/cm^3$ density and an average cell diameter of 86 μm.

Li et al. [26] used polybutylene terephthalate glycidyl methacrylate-styrene (PBT-GS) copolymer chain extender to increase the molecular weight of PET. The modified material was foamed with supercritical carbon-dioxide and this way an average cell diameter of 61 μm was reached.

Coccorullo et al. [27] increased the IV of low molecular weight PET waste from 0.49 dl/g to 0.77 with the aid of 0.75 % PMDA chain extender. The increased molecular weight PET was foamed with CBA, and this way a density of 0.9 $g/cm^3$ was reached that is 36% reduction compared to the unfoamed material.

Xanthos et al. [28][29] also used PMDA to increase the molecular weight of recycled PET bottle material, and reached IV ranging between 0.95-1.13 dl/g. Physical foaming was carried out with $CO_2$, and the density of the created foams was 0.2-0.5 g/cm$^3$ depending on the pressure of the gas introduced into the extruder. The average cell diameter of the obtained foams was between 270 and 340 μm.

Introduction of nucleating agents seems to be inevitable for the production of good quality polymer foams. Nucleating agents have two important roles during foaming. On one hand, they break the homogeneity of the polymer melt, and the created heterogeneous system favors the diffusion and dispersion of the foaming gas, and on the other hand, increase the number of crystal-nuclei formed [30]. Importance of the latter role lies in the stabilization of the cell structure that becomes easier with increasing crystallinity, therefore a mechanically more stable structure can be achieved [31]. The most important parameters of nucleating agents of porous mineral types are their particle size and surface characteristics. The more homogeneous and the smaller is the grain size, the narrower is the cell size distribution and the more stable becomes the cell. While the larger is the surface area, the better gas diffusion and dispersion can be achieved. Generally applied nucleating agents are for instance talc, silicates and chalk [32] [33].

Xia et al. [24] modified PET with an initial IV of 0.80 dl/g using PMDA to reach IV of 0.94 dl/g, and applied montmorillonite (MMT) nanoclay as nucleating agent during base material production. 29-53 μm cell diameter and 10-50 expansion rates were achieved. Well-dispersed clay improved foamability, however increase of MMT content decreased the molecular weight of PET due to degradation induced by the decomposition of the surface treating agent.

The goal of the present research is upgrading of RPET by continuous preparation of low-density foams. In order to prepare suitable raw material for extrusion foaming of RPET, two approaches, chain extender addition and SSP technology were evaluated and compared.

## 2 Materials and methods

### *2.1 Materials*

PET bottle regrind with intrinsic viscosity (IV) of 0.71 ± 0.02 dl/g were supplied by Jász-Plasztik Kft (Hungary).

To increase melt viscosity and IV a styrene-acrylic oligomer multi-functional epoxide chain extender (CE), Joncryl ADR4368C with a molecular weight of 6800 g/mol and an epoxy equivalent weight of 285 g/mol, kindly supplied by BASF SE (Ludwigshafen, Germany) was used.

As nucleating agent HTPultra5 L type talc (T), received from IMI FABI SpA (Postalesio, Italy), with a median diameter of 0.65 μm was used.

### *2.2 Sample preparation*

RPET regrind and regranulates were dried for 4 h at 160 °C in a hot air oven before processing.

Reactive extrusion was carried out in a Labtech Scientific LTE 26-48 twin screw extruder (temperature 240 to 255 °C, rotation speed 100 rpm). Talc, as nucleating agent was added in-situ during extrusion in order to obtain better dispersion.

The SSP reaction was realized with Erema-Vacurema Prime reprocessing technology. In the first step, the PET regrind were dried in a vacuum crystallization dryer at 160 °C for 2 hours. In the next step, the dried and purified material was fed into the vacuum reactor. The

IV increase of the PET regrind took place inside the reactor through solid-phase polycondensation at 210 °C and 5 mbar for 1 hour. Then, the material was melted under vacuum in the directly connected extrusion system. Extruder zone temperatures changed between 280 and 300°C. In this step mixing of talc was not possible, since the fine filter of the vacuum extruder would separate the solid phase from the melt.

$ScCO_2$-aided melt extrusion was performed on a twin-screw extruder (Collin Teach-Line ZK 25T, Dr Collin GmbH, Germany) with a screw diameter of 25 mm and a length to diameter ratio (L/D) of 24. The apparatus consisted of 5 heating zones, $scCO_2$ was introduced into the 4th zone using a syringe pump (Teledyne Isco 260D, Lincoln, NE, USA). $CO_2$ was introduced at the same pressure as the pressure in the extruder. The temperature inside the barrel was regulated at the following six locations: $T_1$-$T_3$ before, $T_4$ at, and $T_5$ behind $CO_2$ injection location and $T_6$ in the die. In the die also temperature of the material ($T_{mat}$) was measured, while the pressure of the material was examined at two sensor locations, right after the injection location ($P_1$) and in the die ($P_2$). In case of materials modified in SSP process, mixing of talc as nucleating agent was realized in this step.

During foam extrusion experiments the screw speed was kept constant at 50 rpm and the following temperature profile was set for the extruder zones: $T_1$= 250 °C, $T_2$= 260 °C, $T_3$= 275 °C and $T_4$= 230 °C, while $T_5$ and die temperature ($T_6$) were varied during experiments. $ScCO_2$ was introduced at a constant volumetric flow rate ranging between 0.5 and 1.5 ml/min. Once $scCO_2$ was injected, a significant decrease in the material pressure within the extruder barrel occurred, mainly due to the decrease of melt viscosity. Parallel with increasing $CO_2$ concentration, $T_5$ and $T_6$ was lowered to increase melt strength in the die, typically to 205-220 °C. Once stable conditions were established, samples were collected.

## *2.3 Methods*

### 2.3.1 IV

Intrinsic viscosity values were determined using a computer controlled PSL Rheotek automatic solution viscometer equipped with optical sensor. Phenol/1,1,2,2-tetrachloroethane mixture in the ratio of 60:40 % was applied as solvent, concentration was 0.5 g/dl, and examination temperature was 30 °C.

### 2.3.2 Capillary Rheometry

Rheological behavior was investigated by SR20 (Instron, USA) capillary rheometer at 270 °C, in the shear rate range of 100-12000 1/s. The preheat time was 300 s. The geometries of capillary dies were: L1 = 5 mm, D1 = 1 mm; L2 = 10 mm, D2 = 1 mm. The real shear stress was calculated by using Bagley-correction, and the real shear rate was calculated by using Rabinowitsch-correction.

### 2.3.3 MFI

Melt flow index was measured by Kayeness Dynisco LMI 4000 device. Temperature was 260 °C, applied load was 1.2 kg.

### 2.3.4 Density measurements

Void fraction of foams was determined by density measurements. 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 (1):

$$V_f = 100\% * \left[ 1 - \left( \frac{\rho_{app}}{\rho} \right) \right] \qquad (1)$$

Density ($\rho$) of the PET based polymer mixtures were considered to be 1.38 g/cm$^3$, 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 (2):

$$\phi = \frac{\rho}{\rho_{app}} \tag{2}$$

### 2.3.5 DSC

Thermal characteristics of the samples were determined with a Setaram DSC131 EVO type DSC device. Heat-cool-heat phases were applied during measurement between 30 and 300 °C, at 20 °C/min heating and cooling rates in nitrogen atmosphere (nitrogen flow of 50 ml/min). Weight of examined samples was between 6-8 mg.

Crystallinity percentage ($\chi_c$) of PET foams was calculated according to Equation (3), where $\Delta H_m$ is the melting enthalpy, $\Delta H_{cc}$ is the cold crystallization enthalpy, $\Delta H_m{}^0$ is the melting enthalpy of a perfect PET crystal equal to 140.1 J/g [34].

$$\chi_c\,[\%] = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m{}^0} \cdot 100\% \tag{3}$$

In case of granulate samples the second heating, when the thermal history is erased, was analyzed, while in case of foams the first heating cycle was examined.

### 2.3.6 SEM

Foam structure was analyzed by Zeiss EVO MA10 scanning electron microscope. Before investigation, samples were coated with gold. Samples were placed in liquid nitrogen for two minutes to achieve cryogenic fracture.

# 3 Results and discussion

## 3.1 *Effect of chain-extension on recycled PET*

During reactive extrusion of RPET regrinds the ratio of epoxide-based chain extender additive was changed between 0 and 1 %. The measured IV and MFI values of the modified RPET regranulates are shown in Fig. 1. The IV values increase linearly with CE content and reaches 0.75 dl/g at 1 %. In parallel, melt flowability shows a decreasing trend in the examined range, at 1 % additive content it decreases to 11 g/10 min. Based on these results, the material modified by 1 % chain extender was chosen for foaming.

Fig. 1. IV and MFI of RPET modified by multifunctional epoxide chain extender

Two different modified materials were produced for foaming: in the one case 1 % CE and 1 % talc nucleating agent was mixed in one step in order to minimize degradation (IV of CE-containing raw material: 0.74 dl/g); in the other case base material was prepared from RPET regrinds in SSP reaction (IV of SSP treated raw material: 0.78 dl/g).

Rheological properties of the materials were tested by capillary rheometer. Cross model (4) was fitted to data points in all cases (Fig. 2.) [35][36].

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0+\eta_\infty}{1+(a_c\dot{\gamma})^{1-n}}\,, \tag{4}$$

where $\eta(\dot{\gamma})$ is the viscosity in the function of shear rate; $\eta_0$ is the zero shear viscosity, $\eta_\infty$ is the infinite shear viscosity (assuming zero in the present simplified case); $a_c$ is a time constant related to reciprocal critical shear rate ($\dot{\gamma}_c$) marking the end of the zero shear rate Newtonian plateau or the onset of the shear-thinning region ($a_c = \frac{1}{\dot{\gamma}_c}$); $n$ is dimensionless exponent.

Fig. 2. Measured data points (at 270 °C) and fitted Cross model curves

Constants of Cross model for the different materials are summarized in Table 1. It can be concluded, that RPET has the lowest zero shear viscosity value which is due to the shorter molecule chain (lower IV value). The zero shear viscosities of the two modified raw materials are higher than that of RPET. Zero shear viscosity of RPET +1%CE+1%talc material differs significantly from RPET after SSP material, however this difference cannot be observed in their IV values. It can be explained by the differences of the two measurement methods. During IV measurement the sample is a dilute solution, which does not include the influence of entanglements [28]. The critical shear strain, which shows the broadness of the molecular weight distribution, determines the end of the Newtonian behavior plateau, and this has the lowest value in case of RPET modified with chain extender, and in case of this material the "n" value is the highest, which refers for higher number of branching [28] [37] [38].

Table 1 Constants and standard error of non-linear regression of Cross model

DSC curves of the second heating of RPET regrind and the two materials produced are shown in Fig. 3, and the characteristic values determined based on the DSC curves are summarized in Table 2.

Fig. 3. DSC curves of the different raw materials

It was found that the glass transition temperature ($T_g$) increased as a result of both molecule chain modification methods, since the mobility of the segments of longer chains is hindered. The crystalline ratio of the modified RPET materials is lower than that of the initial material, due to the more difficult ordering of longer molecules and hence slower crystalline nucleation. It is especially true for the material modified by multifunctional epoxide chain extender, even though it contains nucleating agent as well, in this case the obtained branching molecular structure hinders the assembly of PET chains into crystal lattices [25]. The melting peak temperature of RPET+ 1%CE+1% talc material shifted to lower temperature likely due to the nucleation effect of talc resulting thinner lamellae with lower melting temperature.

Table 2 Thermal properties of RPET regrinds; RPET +1%CE+1%talc and RPET after SSP pellets

## 3.2 *Foaming of modified recycled PET by supercritical $CO_2$*

RPET alone could not be extrusion foamed by supercritical carbon-dioxide method. The obtained foam structure was not stable: cells collapsed due to the insufficient melt strength.

Foaming of base materials improved by two different methods was successful; however production was only stable in a narrow processing window (Table 3). During foaming 1% talc nucleating agent was added to the base material produced in SSP process, therefore its nucleating agent content was the same as that of the other base material. Plasticization effect of $scCO_2$ was significant since even if material temperature was below 225°C in the mold, melt still remained in viscous state.

Table 3 Foam extrusion parameters (rPET+1%CE+1%talc, RPET after SSP +1%talc)

During foaming base materials degraded. IV of formed foams was measured and it was found that IV of RPET+1%CE+1% talc material decreased to 0.71 dl/g (extent of decrease was 0.03 dl/g); while that of material RPET after SSP+1%talc was 0.68 dl/g (0.10 dl/g decrease). The greater reduction of the IV value in the case of the SSP produced base material is likely due to the in situ addition of talc and to the slightly higher processing temperature applied. The longer and more linear molecule chains seem to be more sensitive for the processing conditions.

In order to determine the thermal characteristics of the foams produced, the first heating cycle was analyzed with the aim to examine the thermal history created during production. DSC curves can be seen in Fig. 4, while characteristic values of the two materials can be found in Table 4.

Fig. 4. DSC curves of foams

There is no significant difference between the glass transition temperatures ($T_g$) of the foams produced from the two different base materials. Cold crystallization takes place at 4°C higher temperature and the crystalline ratio is 7% higher in case of PET modified with chain extender. Differences in crystal melting are not significant. If initial crystalline ratio is compared it can be stated that the value of SSP modified material is almost double compared to the material modified with chain extender. The smaller crystallization ability of the latter was already visible when the initial materials were compared, as revealed based on in Fig 3, and is related to the branched molecular structure.

Table 4 Thermal properties of RPET +1%CE+1%talc and RPET after SSP+1%talc foams

SEM images of foams produced can be seen in Figs 5 and 6, respectively. Uniform microcellular structure can be observed in case of both base materials.

Fig. 5. SEM images of RPET+1%CE+1%talc

Fig. 6. SEM image of RPET after SSP+1%talc

Frequency of cell diameters is shown in Fig 7. Cells of foams produced from base material modified by chain extender are smaller and their frequency distribution is narrower compared to foams prepared after SSP process. The higher melt viscosity and the more chain branching enables a more controlled cell enlargement.

Fig. 7. Relative frequency of cell diameters

Compared to the IV value of 0.90-1.40 dl/g reached in former experimental works [28][29][24], the set IV values were in our case relatively low (below 0.80 dl/g), the achievement of which is feasible in case of both processes even under industrial conditions. Still, the $scCO_2$ aided extrusion foaming from the recycled material was successful, foams with similar characteristics as published for original PET in the literature were produced. Table 5 contains the average cell diameter together with the apparent density, void fraction and expansion ratio determined for the materials produced by the two different ways. Foams with apparent density of 0.24 and 0.33 g/cm$^3$ accompanied with an average cell diameter of 213 and 360 μm were manufactured, respectively. In case of the material modified by chain extender additive the foams are composed of smaller cells, resulting in smaller density and higher void fraction.

Table 5 Void fraction, expansion ratio and average cell size of foams (rPET+1%CE+1%talc, RPET after SSP+1%talc)

## 4 Conclusions

The preparation of low density (<0.35 g/cm$^3$) microcellular foams from RPET bottle-regrind by scCO$_2$-aided foam extrusion is demonstrated. In order to prepare suitable raw material for extrusion foaming, the molecular weight of RPET was increased by two methods. Both chain extension through chemical reactions using a chain extender additive and SSP proved to be suitable, however somewhat higher void fraction was reached by adding chain extender. An advantage of SSP process is that food industrial quality can be achieved.

Cost efficient extrusion foaming of RPET using scCO$_2$ does not only offer packaging industrial opportunities through the production and thermo-forming of closed cell sheets but the foamed products are promising to be utilized in the construction industry as insulation materials.

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