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Structure and properties of closed-cell foam prepared from rPET

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Abstract. Nowadays, in the field of packaging technology, one-way polymer packaging materials are increasingly used. Food and packaging industry uses the most, the life cycle of which becomes short, they become waste very quick. Also included are light weight bottles of polyethylene terephthalate (PET). Large amounts of waste can be handled with multiple options. The worst is their dumping on dump sites, as these materials do not compost. Their thermal recycling is more favorable due to their high calorific value, but a real cycle can only be achieved by their physical recycling. However, during the multiple re-purposing, PET's mechanical and processing properties are reduced. In our research, chemical foaming has been investigated, resulting in a smaller weight, better specific property, and fully reusable product. During our investigations, the structure and mechanical properties of recycled PET (rPET) specimens manufactured with different composition, chain and foam additives were analyzed.

1. Introduction

From the 50's onwards, the use of fossil fuels and energy sources increased, which attracted the rapid development of the plastics industry. In 70’s, polyethylene terephthalate (PET) appeared and soon began to dominate the liquid food packaging market. Consumer habits have changed. Due to its low production cost, low weight, good optical properties and gas tightness, PET has outperformed glass [1].

There are chemical and physical possibilities for recycling PET. During the chemical processes, various reactants are used to break the polyester into components which can then serve as a monomer to produce PET and other polymers [2]. By contrast, physical methods are more energy-saving, as they retain the energy invested previously in the material. However, the recycled product is degraded, and its properties deteriorate during use [3].

We want to introduce a property enhancement technology that does not prevent multiple processability. This technology is chemical foaming, this results in smaller weight, better specific properties and a fully reusable product. In our opinion, the chemically expanded structure of recycled polyethylene terephthalate is an appropriate raw material for industrial utilization.

Under the term polymer foam, we mean a two-phase system in which statically distributed variable gas bubbles are embedded in a polymer matrix. Almost all thermoplastics or many crosslinked polymers are suitable to produce a foamed product. Foaming technologies are basically divided into three groups: mechanical, physical and chemical. During the chemical foaming, gases can be formed by the addition of chemical blowing agents which break down when heated, while producing their type-dependent gas (pl. CO, CO₂, N₂, NH₃) [4].

Chemical blowing agents can be either organic or inorganic solids which decompose in the high temperature melt. Their solid decomposition products act as nodules. In addition, large quantities of gas
are generated. The gas bubbles formed at the nodule expand as they cool down, thus form the cells. The formed foam structure is a closed cell, the cavities are well separated from each other, they are not connected, their surface is solid, the cell density is increased towards the core, i.e., structural foam can be adjusted [5, 6].

PET suffers from chain breakage while recycling, which also results in a decrease in the melts viscosity. This causes some difficulties during processing, partly during chemical foaming. Prior to chemical foaming, it is essential to restore the original structure of the raw material. For this purpose, various artificial additives were tested.

Molnár [7] investigated the effect of technological parameters with chain extenders and chemical blowing agents on the injection molded rPET foam. The results obtained during the experiments have shown that the pressure and the switching point significantly affect the foamed structure and its properties. If the pressure drops, the foaming ratio increases with the cell diameters being lowered. Increasing the switch point does not correlate with the total volume of cells, but their average size increases.

Numerous research deals with the effect of chain-extender additives. The effect of the PMDA (Piromellitic Dianhydride) chain extender on the recycled PET extrusion was studied by Raffa [8]. In terms of viscosity, the increasing number of chains increased. In contrast, in the range of lower shear rates, no such difference was seen in the case of higher shear rates.

Toth and his colleagues [9] tested the reaction of recycled PET with radioactive radiation. The base material was reinforced with glass fiber and added a reactive additive. PET scrap was prepared for the experiment and purified to reduce humidity at 540°C for 5 hours. The base material, epoxy additive, was added at 2 m/m%. The additive was Derakane D-410 with a molecular weight of 400 g/mol. Glass fiber was a Zoltek-type E type 10-15 mm long 8 μm diameter product. This was utilized in a 20% weight ratio. During the experiment a radioactive dose was used (10 kGy) to activate the additive. In the tests, bending, tensile, and impact resistance measurements were performed. Because of the bending test, it was found that the bending resistance increased slightly with 20% glass fiber added. In contrast, the additive has worsened the results. In the assay of shock resistance, it was observed that the additive results in a slight decrease again, while the irradiated dose can improve impact resistance. Because of the research, they received a quality-enhanced material. The original PET impact resistance was exceeded by the new reactive reinforced recycled PET. This could be a major milestone in the secondary use of PET.

Coccorullo and his colleagues [10] have tested for the molecular weight increase in the chemical blowing agent with PMDA and CT 534 (Hydrocerol) as excipients. PMDA is a by-product free, economically feasible additive. To avoid crosslinking, it is not advisable to use more than 0.2-0.3% of the additive in the mixture. A closed cell structure can be formed with the use of the appropriate amount. The primary purpose of the research is to produce high-density structural foams from low viscosity raw materials. The secondary aim is to create the right tool in which the foaming process can be reproduced, while changing the various parameters, the foam structure can also be modified.

Ronkay et al. [11] wish to increase the impact resistance with rubber-tight additives. Rubber-tight additives are filler particles which preferably provide a small film thickness with uniform dispersion. The functionalized end group of reactive additives improves its attachment to the PET matrix and provides a better distribution by changing the interface energy between the matrix and the additive.

2. **Applied materials and methods**

During the experiments, commercially available blue crystallized PET regranulate (rPET) was used. Our chemical blowing agent (CBA) was Tracell IM 7200, which was mixed with 4% of the raw material. Due to their high moisture absorption, hygroscopic plastics, such as PET, must be dried, especially before injection molding. The moisture content of the PET should not exceed 0.004% during processing. In this experiment, the base material was dewatered in a DEGA 2500 drying chamber to achieve this. Prior to extrusion, the recycled PET was dried for 24 hours in the drying chamber at 100°C. After extrusion the mixture was dried for another 12 hours at 140°C in the hot air-drying chamber. In the
experiments, CESA Extend was used as a chain extender (CE) at a rate of 2%, while the Du-Pont Elovaloy PTW was used as an impact modifier (IM) additive at 10%. The exact composition and marking of the manufactured blends are given in Table 1.

| Composition of the injection molded products | rPET [%] | CE [%] | IM [%] | CBA [%] |
|---------------------------------------------|---------|-------|--------|---------|
| rPET (reference)                            | 100     | 0     | 0      | 0       |
| rPET4CBA                                    | 100     | 0     | 0      | 4       |
| rPET2CE4CBA                                  | 100     | 2     | 0      | 4       |
| rPET2CE10IM4CBA                              | 100     | 2     | 10     | 4       |

The Arburg ALLROUNDER 420C Golden Edition injection molding machine was used to produce the specimens. To achieve the appropriate foam level, the pressure differences can be influenced by the breathing mold technique. During this process, the polymer mixed with the chemical blowing agent is injected into the mold cavity where the compact surface layer of the piece is formed during the cooling. Then, by minimally opening the tool, the space increases, the pressure decreases, hence the melt forms into the blown material inside as foaming takes place. During the cycle a 0.3 mm mold opening was used (Fig. 1) (Table 2).

![Figure 1](#)

**Figure 1.** The injection molding cycle used with the breathing mold technique [12]

The specimens were produced with mold temperature of 35°C. The foam structure of the manufactured specimens was tested by YXLON Y.CT Modular Industrial Computer Tomography (CT). The impact resistance was measured on CEAST 65-45.000 impactor with 4 J hammer, 62 mm support span by the EN ISO 179 standard. The tensile test was done on the INSTRON 5582 universal tensile machine. The specimen were pulled at 1 mm/min tensile speed with 100 mm support span. To determine the modulus of elasticity, if the elongation reached the 1% value, it was switched to 5 mm/min. Measurements were carried out in accordance with EN ISO 527. Flexural tests (three-point bending
tests) were also carried out on the INSTRON 5582 universal tensile machine according to EN ISO 178. During the test, the specimens were bent at 10 mm/min with 64 mm support span. Five assays were performed at room temperature with relative humidity of 50%; for each, averaging and standard deviation were calculated.

| Table 2. Injection molding parameters |
|--------------------------------------|
| **Unit** | **Value** |
| Clamping force | kN | 150 |
| Nozzle temperature | °C | 260 |
| Injection pressure | bar | 650 |
| Injection speed | cm³/s | 30 |
| Pack pressure | bar | 150-50-20 |
| Pack pressure time | s | 2-1 |
| Mold opening | mm | 0.3 |
| Cooling | s | 20 |
| Mold temperature | °C | 35 |

3. Results and discussions
In the case of injection molded specimens, we examined the characterization of the foam structure, the density of the products and the mechanical properties. The following subsections describe the results obtained.

3.1. Density
When determining the density of solid substances, the weight recorded in a known density liquid is compared to the mass measured in air. During the measurement, first determine the mass taken in air and then the mass dipped in the reference fluid. Density was determined in 98% ethanol using an Ohaus Explorer scale, based on Equation (1).

\[
\rho_{\text{calc}} = \rho_{\text{ethanol}} \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{ethanol}}}
\]

(1)

where \(\rho_{\text{calc}}\) [g/cm³] is the density of the measured specimen, \(\rho_{\text{ethanol}}\) [g/cm³] is the density of ethanol [g/cm³], \(m_{\text{air}}\) [g] is the weight of the specimen in air, \(m_{\text{ethanol}}\) [g] is the weight of the specimen in ethanol.

One of the beneficial effects of foaming is weight loss. Because of the established cell structure, the density of the test pieces decreased. The average drop in density was 8.27%. In the case of a functional group mixed only with a chain extender, it can be said by increasingly adding chain extender to the mix it marginally effects the density (1.34%). In addition to the impact modifier, the density increased, but still did not reach the pre-foam density value (Fig. 2).
3.2. Morphology

During the test, we analyzed a 2 mm height segment of each specimen. On a test piece, several measurements gave the average of the results. During our testings, 1280 images/360° were taken.

When the 3D CT recordings of the test specimens are jointly examined, the effect of the chain extender on the cell structure is conspicuous (Fig. 3). In addition to the additive, a true foam structure is formed. The impact resistance increased the skin thickness, but there was no suction on the outer surface of the test piece.

Concerning porosity, it can be observed that the rate of foaming has fallen due to the chain extender, but the mixture reacted well to the impact modifier (Fig. 4).
3.3. Mechanical tests

We have investigated the effect of different blends on mechanical properties. The results are summarized in Table 3.

The tensile properties of the dumbbell specimens, using various additives were tested. The tensile modulus has increased due to the chain extender as an ordered cell structure has been achieved. Due to the impact modifier, the specimens lost their elasticity. The tensile strength improved by 19.28% due to the chain-extender masterbatch. Using the impact modifier, we achieved a 26.49% increase.

The flexural modulus of the specimens was reduced by the chain extender, but the impact resistance increased 14.55%, when compared to the results of the original foamed pieces. A 30.04% increase can be observed in the chain extended test pieces. The deviation values were high. Based on the results, it can be said: the flexural modulus can be increased using the impact modifier. During the tests, the flexural strength of the chain extended specimens was reduced. This is due to the increase in cell density. Due to the better cell distribution, the cell number increased while using the masterbatch. The flexural modulus has fallen to nearly a quarter of this. When adding impact modifier to the mix, we could see the improvement. A 62.16% increase was observed compared to the only chain extended test specimens. However, with the use of the two masterbatches, we did not achieve the results of the foam without additives.

The specimens lost their impact resistance by applying the chain extender agent. In addition to the impact modifier, Charpy's impact strength showed an improvement of 45.12%.

Table 3. Mechanical properties of the injection molded specimen

|          | Tensile test | Flexural test | Impact test |
|----------|--------------|---------------|-------------|
|          | $E_T$ [GPa]  | $\sigma_T$ [MPa] | $E_F$ [GPa] | $\sigma_{1,5h}$ [MPa] | $a_N$ [kJ/m²] |
| rPET     | 4.58±0.03    | 50.03±1.48    | 7.47±0.61   | 67.14±0.65     | 3.45±0.38    |
| rPET4CBA | 1.32±0.24    | 19.92±3.92    | 3.64±0.57   | 40.39±1.26     | 1.50±0.10    |
| rPET2CE4CBA | 1.35±0.33   | 24.68±0.63    | 2.98±0.56   | 13.05±1.61     | 1.22±0.38    |
| rPET2CE10IM4CBA | 1.35±0.07   | 27.10±1.89    | 4.26±0.54   | 34.49±2.07     | 2.34±0.31    |

Generally, the resistance to wear has been reduced by a chain extender, however the cell structure has improved. The effectiveness of the impact modifier has been verified by several tests. With the use of the two additives, the resistance to mechanical stress increased and the cell structure improved.

4. Industrial application

The experiment presented is to reproduce the inner door handle of an automobile, from foamed rPET. For this we used the rPET2CE10IM4CBA blend we thought was best for this purpose.

We examined the width and height of the handle part of the injection molded internal handle using a caliper. Twenty samples were manufactured and parameterized, marking the number of work pieces tested. The tool is suitable to produce both the right and left side door handle. A total of 85 internal door handles have been created in automated production. Two 5-piece group of specimens were chosen for my examination. Approximately 23 minutes passed between the two groups. As a condition for reproducibility, a tolerance of 0.1 mm was determined for both the width and the height tests.

When measuring the height of left-hand handle, we got an average of 8.55 mm with a 0.019 mm standard deviation. Thickness measurement resulted in an average value of 14.55 mm and a 0.013 mm standard deviation. All test pieces have performed within the tolerance set by us.

When analyzing the height of the test pieces on the right-side cavity, an average rating of 8.55 mm was obtained with a 0.019 mm standard deviation. The width test resulted in an average value of 14.54 mm and a 0.019 mm standard deviation. These values are within the tolerance range. Based on the measurement data, it was found that the reproducibility of the product is not affected by filling the right
or left cavity because they are mirror-symmetric to each other. On the average width of the pieces 0.01% and 0.07% in length were measured. As a result of the investigation, it can be concluded that there is no difference between the right and the left door handle specimens during the production of the pieces. Using the tolerance field defined, we found that the piece is perfectly reproducible.

To analyze the reproducibility, the internal door handle was tested on an optical 3D coordinate measuring system (GOM) (Fig. 5). The resulting three-dimensional model was compared to the CAD model used in tool making. The joint was below 0.004. Due to this, it can be said the product can be manufactured using injection molding and a breathing mold technique.

![Figure 5. GOM test result of the internal door handle](image)

By analyzing CT scans, it can be concluded that higher cell diameters were generated during the production due to the increased volume (Fig. 6). Cell density and cell distribution resulted in a suitable foam structure.

![Figure 6. CT scan of the internal door handle](image)

5. Conclusion
During our work, we aimed to recycle the ever-increasing amount of PET bottle waste by chemical foaming so as not to deteriorate its subsequent recycling properties. After the measurements and production, we found that the available crystallized blue bottle regranulate is suitable for producing a closed cell integral foam product. After testing the use of various additives, we can improve the resistance of the material against mechanical stresses. The new blend can be widely used in the automotive and construction industry.
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