Flame retardancy of recycled PET foam

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Abstract. Although significant marketing efforts have been made in recent years to reduce polymer use, the number of plastic bottles being discarded is increasing worldwide. The global environmental-socio-economic problem posed by polyethylene terephthalate (PET) bottles can only be solved by expanding large-scale recycling opportunities, while reducing the use of pure raw materials. In this article on the large quantities product of PET was upcycled with chemical foaming. During the experiments 2 m% chain extender and 4 m% chemical blowing agent and different amount of brominated flame retardant was used. The invested materials were examined with standard mechanical tests, scanning electron microscopy and UL-94 standard flammability test. After the investigation it was found that the crystallized blue PET bottle re-granulate can be used forming a flame retardant closed cell foam structure.

1. Introduction
The use of PET, due to its properties, is most noticeable in the packaging industry. Its low density, transparency, impact resistance and carbon dioxide barrier make it the most important raw material for the packaging industry. However, one-way packaging materials become very quickly waste and have a serious impact on the environment. The natural degradation of PET is over half a thousand years. Therefore, the need for recycling PET waste is permanently increasing [1].

Due to the unmanageable nature of solid plastic waste, its volume is constantly increasing and burdens the nature. In Europe, the volume of collected PET bottles participating in the greenhouse effect increased from 0.2 Mt in 1998 to 1.26 Mt in 2008, with an annual growth rate of 19% [2]. In 2016, the number of PET waste increased to 9.6 Mt. According to current forecast, by 2021 only PET bottles will account for 11.6 Mt worldwide [3].

The primary solution to the environmental burden of PET bottles is the production from recycled materials. PET recycling involves three different chain breakage, which can occur as a result of mechanical- and thermal loading and hydrolysis [4]. This behaviour is a serious problem when using recycled polyethylene terephthalate (rPET) as the quality of both the raw material and the finished product is deteriorated. In our experiments, chemical foaming is used to form an integral foam structure from waste bottles using a conventional injection moulding machine. In the case of PET, the foaming depends mainly on the IV value of the base material, since the viscosity of the molten material to a large extent influences the formation of the foam structure. Limits for foam structure formation are found in the literature to be above of 0.8 dl/g, whereas for low density foams require an IV value above 0.95 dl/g. Thus, it is essential to formulate a chain extender to foam rPET [5].

Coccorullo et al. have used a chain-extender additive in their PET recycling research for better applicability. Due to the low IV value of the starting material (0.48 dl/g) it was not suitable in its
original state. As a result of their experiments, it has been found that the increasing use of a chain extender increases the viscosity of the molten material, while at higher shear rates, small differences in the ratio of the chain extender additive are found. In their experiments they were able to increase the IV value of the starting material by 37.7% [6].

The amount and rate of chain-extender additives were also investigated in case of rPET by Turfa et al. The use of 1% additive is sufficient to increase the length of the polymer chains, but at 2% the frequency of branching within the molecular chain also increases. At higher rates of application, unwanted crosslinking is caused by the chain extender, which can lead to crystallisation leading to degradation of processing properties [7].

Compared to extrusion foaming [6-9], the production of injection moulding foamed products is a less researched area. During the production of the foam structure on the injection moulding machine, the porosity is greatly influenced by the injection moulding parameters.

Gómez et al. investigated the effect of injection moulding parameters on glycol modified polyethylene terephthalates (PETG) microcellular foam structure. Their results show that the tool temperature and the batch volume have the greatest influence on the foam structure formed. It has been shown that increasing the tool temperature increases the porosity of the samples [10].

If the foam structure of rPET is to be widely used, care must be taken to reduce the rate of inflammation and flame propagation. The main raw material for polymer production is petroleum, so the calorific value of the products is almost the same (40-45 MJ/kg). The primary purpose of incorporating flame retardants is to reduce flammability [11].

In their research, Bocz et al. investigated the development of flame retardant, fabric reinforced composites from mixed plastic waste. During their work, the research team has developed a multilayer, value-added composite based on high polyolefin-containing automotive shredder light fraction. The mechanical properties of the recycled composites are provided by the fabrics made of polypropylene. The reduced flammability is provided by a matrix layer of secondary raw material, a phosphorus-containing flame-retardant additive. Based on the results, it was found that high technical value plastics, which can be recovered from secondary raw materials, were eventually obtained by self-reinforcing composite with added flame retardancy [12].

Xue et al., in their research, produced magnesium hydroxide and poly (ethylene terephthalate) microencapsulated CMSs by polymerization and liquid phase deposition. The PET used was produced by blending with the flame retardant using a direct molten blend. Based on their results, the developed material showed a LOI of 27.2%. Developed CMSs suppress smoke production [13].

The design of the foam structure affects the flammability of the plastics. An important task in developing the foam structure is to increase the resistance to combustion. In their research, Wu et al. developed a novel and simple strategy for the composite material of high flame-retardant polymer foams using a silicone resin coating and a silica gel self-extinguishing layer. An organic / inorganic silicone polymer coating was formed on the surface of the polymer foam based on condensation polymerization and they were able to minimize the oxygen concentration. During the UL94 test, the developed foams completed a complete self-extinction within 30 seconds.

In their research, Carosio et al. investigated the layered structure of flame retardants in a closed cell foamed PET structure. The flame-retardant properties of ammonium polyphosphate (APP) have been compared with that of deoxyribonucleic acid (DNA). Inflammation and cone calorimetry studies clearly demonstrated the superior performance of APP-coated coatings over DNA-based coated foams. As a result of their experiment, they have found that APP-based coatings can suppress the melt-drip behaviour characteristic of PET and that they develop a 25% reduction in heat release peak [14].

At the beginning of our research the aim was to produce recycled PET integral foam structure by chemical foaming. As a result of the first experiments, we managed to produce closed cell foam on a conventional injection moulding machine using chemical blowing agents [15]. In order to improve the foam structure, the ability of various foaming agents to form the foam structure of rPET was tested. Degradation due to chain breakage greatly reduced foam formation; we increased the length of the molecular chains using CESA Extend. To improve the mechanical strength of the foam structure, 10%
impact modifier additive was added to the blend, which improved the Charpy impact strength by 18%.

As a further development of the material, various flame retardants have been tested to improve the flame resistance of the foam [16]. The results of the new blend showed that even a small amount of flame retardant improved the Charpy impact strength of the samples by a considerable amount. The flame retardant increased the porosity of the samples and reduced the cell diameters, so the results of all mechanical tests were modified with the addition of the additive. Thus, the additive used for flame retardancy showed a greater improvement in the mechanical properties of the blend than the master blend for impact resistance [17]. Based on the results, the question raised; is there a need to use impact modifier during manufacture? In this article, we investigate the properties of rPET foam developed with the use of a flame retardant without the addition of impact modifier.

2. Applied materials and methods

The used matrix material was the blue crystallized PET regranulate (rPET) which supplied by Fe-Group Invest Zrt (Hungary) (intrinsic viscosity (IV) 0.8 dL/g). The used chain extender additive was CESA Extend NCA002531-ZA that provided by Clariant (Switzerland), which contains Joncryl ADR 4368 type epoxy-based styrene-acrylic multifunctional oligomer reagent. The used flame retardant additive was ICH Fl. Ret. 01904 which donated by ICC-Chemol (Hungary) with 85% dispersion of brominated organic compound in ethylene co-polymer. The used chemical blowing agent was Tracell IM 7200 that granted by Tramaco (Germany) endothermic compound with 120 ml/g gas expansion and 70% blowing agent content.

The matrix was dehydrated for 6 h at 120 °C, and then blended with the additives. The twin-screw extruder type LT 20-440 (Thailand) was used for the melt mixing with 265 °C melt temperature. The produced re-granulate was dehumified for another 6 h at 120 °C, then 4x10 mm² cross-section dumbbell-shaped specimens were prepared by an Arburg Allrounder Advance 420C Golden Edition (Germany) injection moulding machine with breath moulding technique, with 265 °C melt temperature, 45 cm³/min injection speed and 35 °C mould temperature. The injected dumbbell-shaped specimen was used for tensile and flexural test. For impact test both ends were cut off to get standard 4x10x80 mm specimen. The SEM images were took from the fracture surface of impact test specimen. For UL-94 test the dumbbell-shaped specimen's one end was cut off. Table 1 shows the composition of the test samples. The notation B used indicates that this is a continuation of an earlier series of experiments, the results of series A are in our earlier publication [17].

| Table 1. The compositions of the test samples |
|---------------------------------------------|
| ref  | B-0 | B-5 | B-10 | B-15 | B-20 |
|------|-----|-----|------|------|------|
| rPET | 100 | 100 | 100  | 100  | 100  |
| Chain Extender | 2 | 2 | 2 | 2 | 2 |
| Chemical Blowing Agent | 4 | 4 | 4 | 4 | 4 |
| Flame Retardant | 0 | 5 | 10 | 15 | 20 |

The melt volume rate (MVR) was determined using a modular MVR tester type Ceast MF-30 (Italy) with 2.16 kg load at 210 °C. The density was determined based on the Archimedes principle using analytical balance type Ohaus Explorer (USA). The inner structure of parts was investigated with a Jeol JSM 6380LA (Japan) type scanning electron microscope (SEM).

The EN ISO 527 standard tensile tests were executed using universal testing machine type INSTRON 5582 (USA) with 100 mm grip length and 1 mm/min test speed when determining the modulus and 5 mm/min when determining the strength. Three-point-bending tests were carried out using universal testing machine type INSTRON 5582 (USA) as stated by EN ISO 178 standard with 10 mm/min test speed and 64 mm support span. Charpy impact tests, as claimed by EN ISO 179 standard, were conducted by impact equipment type CEAST 65-45,000 (Italy), using unnotched specimens, with a pendulum of 15 J and 62 mm support span.
For the determination of mean value and standard deviation five specimen was used in case of every test. The tests were performed at room temperature with relative humidity of 50%.

Standard UL-94 tests were implemented in a chemical fume hood with methane gas on 4 mm thickness specimen. UL-94 classification is used to determine dripping and flame spreading rates. First, vertical burning tests were carried out. If the samples did not reach any class (V-0, V-1 or V-2), then the horizontal burning test was conducted as well.

3. Results and discussions
The following section presents the test results for the samples. The aim of our study was to analyse the effect of the flame retardant on the formation of foam structure and its mechanical properties.

3.1 Morphology
The foam structure is highly dependent on the fluidity of the material. In the 1. figure, sample densities are compared with MVR values. The results show that the density of the samples increases with increasing flow rate.

Increasing the proportion of flame retardant, the density increased steadily. This contrasts with the results of samples produced with impact resistance enhancers. Increasing the proportion of flame retardant, fewer cells were formed in the material. This suggests that, although the impact modifier itself did not promote foaming, it had a significant effect on the flowability of the material when mixed with the flame retardant. The MVR value of the samples with impact modifier increased continuously with increasing the flame retardant ratio, thus increasing the viscosity of the blends in inverse proportion [17]. In contrast, the viscosity of the presently tested blends shows a steady decline as the rate of flame retardant increases. Samples with a lower MVR value of 5 m% (B-5) and 10 m% (B-10) flame retardant, respectively, showed greater loss of density than previous samples with impact modifier.

![Figure 1. The melt volume rate effect on density of the different flame retardant content samples](image)

Comparing the density and flow rate results with the fractures microscope images (Fig. 2.) shows that not only did the cell number decrease with the increase of the flame retardant ratio, but also the cell diameters increased. The large reduction of the density in the samples containing 5 m% (B-5) and 10 m% (B-10) flame retardant was greatly influenced by the thinner shell of the samples. The melt in contact with the temperature of the tempered tool wall is continuously solidified to form an external pore-free shell. The skin layer on the sample containing 10 m% (B-10) flame retardant is less than half that of the samples containing 20 m% (B-20) flame retardant. For mixtures with lower MVR values, a more ordered cellular structure is obtained, and indeed an integral foam is formed in which the expansion ratio increases towards the centre of the section.

Fragmentation of the samples can be compared to the measured density values. Lower flow rates resulted in higher porosity and more ordered cellular structure. Even with higher flow rates, less cells
with large diameters were formed. There is a risk of damage to the closed-cell foam structure as the foam formation of mixtures with lower viscosity may cause the cells to join.

![Figure 2. The SEM micrographs of the fracture surface of the different flame retardant content samples](image)

### 3.2 Mechanical properties

The foam structure forming turns the tough material brittle. The results of the tensile test are shown in Figure 3. The results indicate that the chain extender had a positive effect on both tensile strength and Young modulus. The primary reason for this is that the use of a chain extender by coupling the molecular chains facilitated the formation of a closed cell foam structure. A more ordered cell structure was obtained than with no additive, which is supported by the lower standard deviation. The results of the study show that although the value of the modulus of elasticity increased due to the high value of the standard deviation, there is no significant difference between the results of the flame retardant samples. The higher modulus of elasticity can be related to the lower cell number seen on SEM images. Samples with 15 m\% (B-15) flame retardant with the highest modulus of elasticity had a small number of cells with uneven distribution. The distance between the cells was the largest on these samples. As a result, while samples with high porosity were rapidly fractured, samples with low cell number were capable of elastic deformation.

![Figure 3. The effect of flame retardant to tensile properties](image)

The results show that the tensile strength of the samples containing the flame-retardant is continuously decreasing with increasing the proportion of flame retardant. The standard deviation of the samples containing 15 m\% (B-15) and 20 m\% (B-20) flame retardant was high even with the use of chain extender. During the test, several samples had joined cells. This can be related to the higher...
MVR value. In the test, joined cells facilitated rupture as stress collection areas, even though these samples had a much larger shell thickness. As a result of the thinning or rupture of the intercellular material, the whole sample soon broke. The high standard deviation values are also due to these incomplete cells.

The more arranged foam structure observed in the samples containing 5 m% (B-5) and 10 m% (B-10) flame retardant, respectively, resulted in a reduction in the inter-sample variation in both tensile strength and elastic modulus results. The results indicate that the use of the flame retardant had a negative effect on the tensile stress resistance of the material.

The results of the three-point bending test are shown in Figure 4. The foamed samples of rPET soon underwent brittle fracture after minimal bending. The use of flame retardant reduces the results of the bending elastic modulus. The results of the bending test can also be compared with the shell thickness seen on the fracture images. Both the flexural modulus and the flexural strength were greatly reduced using a chain extender. In contrast, a more ordered cell structure resulted in lower standard deviation values during sample analysis.

At B-5 and B-10 samples high cell density foams showed low flexural modulus. During the three-point bending test, the thick shell showed greater elastic deformation. Another reason is that where the samples containing 15 m% (B-15) and 20 m% (B-20) flame retardant still form a thick solid shell, for the samples containing 5 m% (B-5) and 10 m% (B-10) flame retardant, only the intercellular matrix material can withstand the stress. These thin solid units crack between the cells so that the elastic deformation of the specimen itself is lower. In contrast, their flexural strength is much higher for samples with larger shells containing 15 m% and 20 m% flame retardant, respectively. This is due to the larger cell diameter experienced with the higher flame retardant content and to the joined cells. As a result of the stress, samples with larger cavities suffered fractures with low flexural strength in which the highest standard deviation was observed.

High cell density B-5 and B-10 specimens were broken only after cracking and breaking of matrix between cell units, resulting in higher flexural strength values.

If samples without a flame retardant are considered, the use of a chain extender, while providing a more ordered cellular structure and higher porosity, results in approximately one-third of the flexural strength of the samples. At this value, the use of a flame retardant at 5 m% (B-5) also showed a more than fourfold improvement. This can be paralleled with MVR values at lower flame retardant contents. The absence of impact modifier had a positive effect on the flexural strength of the material because the additive increased the stiffness of the samples.

![Figure 4. The effect of flame retardant to flexural properties](image)

In our research results, the application of impact modifier has reduced the resistance of the samples to tensile and flexural strength. In contrast, improved impact strength in Charpy impact test [17]. The results of samples prepared without impact modifier are illustrated in Figure 5. The figure shows that the use of a chain extender, which has resulted in a higher cell density, nearly halves the impact strength of the specimens. Contrary to increasing the flame retardant ratio, the Charpy impact strength of the samples is reduced. Based on the fracture recordings, the chain extended samples result in fast fracture
due to the high porosity. Even samples with a 15 m\% (B-15) and 20 m\% (B-20) flame retardant with a thick skin layer have low toughness. This can be compared to thinned cell material, which decreased in proportion to the increase in MVR.

The high standard deviation observed during the measurements is primarily due to the disordered cell structure. In the test, the foamed PET specimens produce high dispersion in all cases. This is due to the cell density in the middle section and the size of the cell diameters. If we consider the cell distribution seen on the SEM images, we found that the 15 m\% flame retardant (B-15) had the lowest cell density in the middle section.

**Figure 5.** The effect of flame retardant to impact properties

### 3.3 Flammability properties

The samples were subjected to the UL-94 flammability test (Table 2.). We started the study with the more rigorous vertical burning. All samples were degraded by drip burning during the study. Thus, samples containing 15 m\% (B-15) and 20 m\% (B-20) flame retardant, respectively, only met the criteria for classification V-2. This can be compared to the high MVR value measured during the flow test. All in all, it can be concluded that although the impact modifier does not have a direct effect on the material's resistance to burning. The application increases the viscosity of the samples, resulting in thickening of the intercellular areas, which play a major role in the quenching process. A large volume of burning was observed during the heat transfer, which also dripped from the sample. In contrast, samples with impact modifier agent exhibited much lower levels of degradation due to the release of bromide free radicals from cell walls. Furthermore, the lower MVR value reduced the possibility of dripping. Thus, these samples met the requirements of flammability class V-0 [17].

| Samples | UL94 rating | Burning rate (mm/min) |
|---------|-------------|-----------------------|
| ref     | No rating   | -                     |
| B-0     | No rating   | -                     |
| B-5     | HB          | 19.5                  |
| B-10    | HB          | 16.2                  |
| B-15    | V-2         | -                     |
| B-20    | V-2         | -                     |

Samples containing 5 m\% (B-5) and 10 m\% (B-10) flame retardant could not be classified in the vertical test. Therefore, they were subjected to the UL-94 test in a horizontal configuration. The B-5 sample burned at 19.5 mm/min while the B-10 sample burned at 16.2 mm/min. None of the specimens reached the maximum burning rate of 40 mm/min and therefore the samples can be classified in the HBF flammability class. Overall, it can be stated that B-5 or B-10 material may be suitable for
industrial use, but its use is limited. The non-flame retardant rPET foams could not meet the criteria for any classification.

4. Conclusion
After analysing the specimens, it was found that the available crystallized blue bottle re-granulate can form a closed cell foam structure with flame-retardant, without the use of impact modifier. In contrast, the impact modifier plays an important role in the foam texture because it influences the flowability of the blends. The impact modifier reacts with the flame retardant during extrusion and doubles the viscosity of the blends. In the higher viscosity material, the solid matrix between the gas cells formed by the carbon dioxide is not damaged, thus providing a closed cell foam structure. By omitting the impact modifier, the cells combine in the high flow samples. Thus, in the samples containing 15 m% (B-15) and 20 m% (B-20) flame retardant, the merged large cells formed cavities that function as a stress collection point. However, around such a large hole, the matrix formed a thick solid unit. As a result, the overall density of the samples hardly decreased. On the other hand, mechanical tests showed a steady decline with the increase of the flame-retardant ratio. The disordered cellular structure formed also reduced the resistance of the samples to burning. In addition, the high MVR in the UL-94 tests resulted in drip burn, so that even a 20 m% flame retardant sample (B-20) could only meet the criteria of the V-2 flammability class. The results achieved are moving in the right direction for the E&E industry, for example injected TV parts [18], but further development is still needed.

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