Development of flame retarded composites of reduced additive content for upgrading of recycled PET

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Final report

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1. Introduction

The increasing PET bottle usage produces an enormous amount of PET waste, the handling of which is an actual and urgent challenge. The currently widespread simple thermomechanical recycling is, however, accompanied with significant property damage (downcycling). The main causes of downgrading (poorer quality and reduced functionality) of the reprocessed PET are the less transparency and the significantly decreased rheological and mechanical properties caused by the thermal and hydrolytic degradation during thermomechanical reprocessing. Additionally, there are economic constraints hindering the recycling of PET waste; the products obtained by conventional thermo-mechanical reprocessing do not meet the requirements of the market neither in terms of mechanical properties nor in aesthetic aspects. Therefore, the currently produced recycled PET products, such fibers, are almost unmarketable, which negatively affects the motivation for recycling. The solution for this negative tendency could be the transformation of the low-cost PET waste into valuable composites or products that have special functions or properties, such as outstanding strength, impact resistance, and heat and/or fire resistance.

2. Results

2.1. Investigation of morphology of original and recycled PET

The main problem during processing recycled PET is degradation. The drop of the average molecular weight has a significant effect on the morphological properties, and parallel with on the mechanical properties, too. The elasticity and the impact resistance of the product decrease significantly. This limits the application of the secondary material. In late studies the three-phase model is used to investigate the morphological structure of PET. According to this model, PET has a crystalline (CRF), mobile amorphous (MAF) and rigid amorphous fraction (RAF). Rigid amorphous fraction is assigned the crystalline interface.

The aim of research was to produce injection molded samples from recycled PET with different processing parameters. The morphological properties of samples were analyzed by MDSC measurements. Different crystallization (cold-crystallization, non-reversing crystallization) and melting (reversing melting, non-reversing melting, total melting) were determined and compared from total-, reversing- and non-reversing heat flow signals.

During DSC measurements, total-, reversing- and non-reversing heat flow signals were registered. In the course of evaluation following peaks were investigated and compared: cold-crystallization (CC, between 100-130 °C) and melting (M, 210-270 °C) peaks on total heat flow signal, melting (RM, 130-270 °C) peak on the reversing heat flow signal, crystallization (NRC, between 130-270 °C) and melting (NRM, 210-270 °C) peaks on non-reversing heat flow signal (***Figure 1***). The overlapped crystallization and melting peaks between 130-270 °C on the non-reversing heat flow signal were separated by Calisto software (Setaram, France).

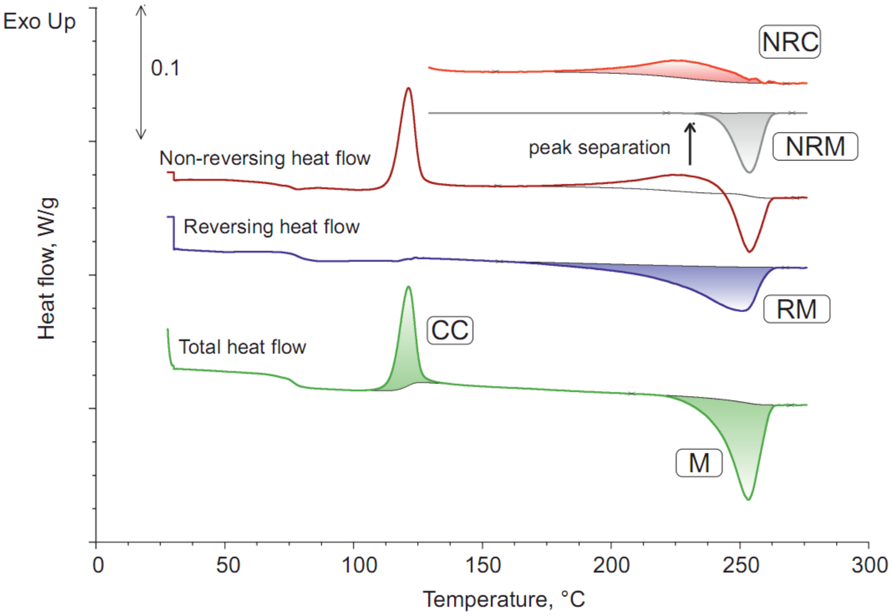
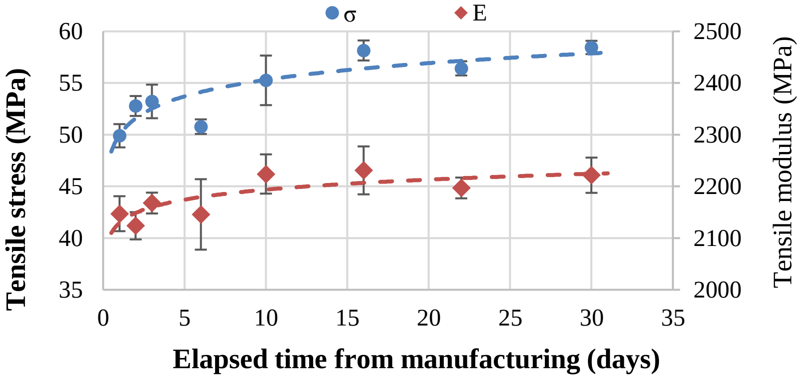


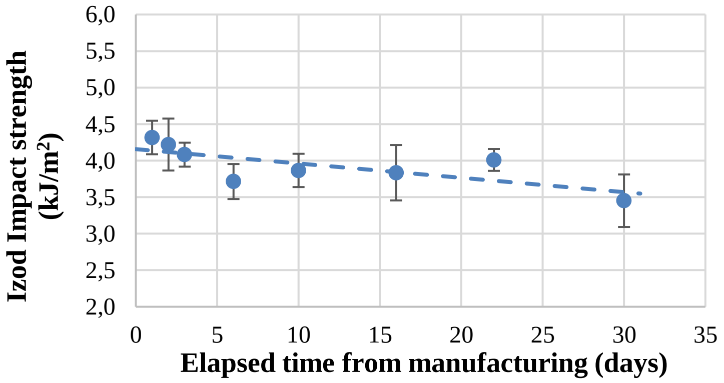
Figure 1. *Measured heat flow signals and investigated peaks (NRC: non-reversing crystallization, NRM: non-reversing melting, RM: reversing melting, CC: cold-crystallization, M: melting)*

Relationships were found between crystallization and melting processes: the initial crystallinity equals to the non-reversing melting, and the post-crystallization processes equals to reversing melting. In the case of PET, during different crystallization processes (crystallization during manufacturing, cold-crystallization, post-crystallization) different structures can be formed (e.g. different crystalline size, perfection of the structure), which can lead to different mechanical properties (e.g. tensile strength, impact strength). The deeper analysis of crystallization processes can help to understand better the morphological properties which have a significant influence of the mechanical properties of products.

In the next step morphological and mechanical properties of injection molded recycled PET samples were investigated. Recycled PET was made from original PET by extrusion. Plate samples with 2 mm thickness were injection molded. The morphological structure of the regranulates and the samples were determined by DSC measurements, using the three-phase model. The mechanical properties were determined by tensile and impact tests (***Figure 2***).



a)



b)

Figure 2. *Tensile properties of the samples (**a**); Impact strength of the samples (**b**)*

The crystalline fraction of the injection molded samples increased significantly after the produce. During the post-crystallization the chain segments of the RAF increase the CRF, in the skin layer from 4% to 10%, in the core layer from 4% to 12%. The MAF can be increased by realignments of the chain segments in the RAF, due to breaking and evolving secondary bonds.

The tensile strength increased which can be caused by orientation of the MAF and increase of the CRF. The tensile modulus increased as well which is caused by orientation of the MAF during the post-crystallization. The impact strength decreased significantly due to decrease of the elasticity of the samples, and increase of the crystal sizes.

Significant changes can be observed in the structure of the core part of the specimens in the four weeks after manufacturing. If the rigid amorphous fraction is assumed to be between the folding surfaces of the crystallites and the mobile amorphous regions, the results refer to a post crystallization process that took place after manufacturing, i.e. rigid amorphous chain parts increased crystalline size, and therefore crystalline fraction as well (***Figure 3***). During chain rearrangement process, secondary bonds may break (e. g. since chains approach a state of equilibrium), and parallel with this new bonds may form. If the amount of the broken secondary bonds is higher than that of the formed bonds in the interphase of the rigid and mobile amorphous fractions, it can increase the mobile amorphous fraction as well (***Figure 4***).

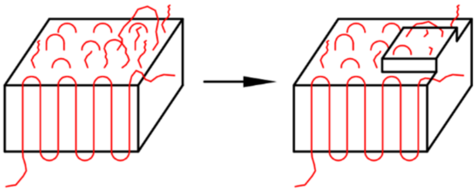


Figure 3. *Process of post crystallization*

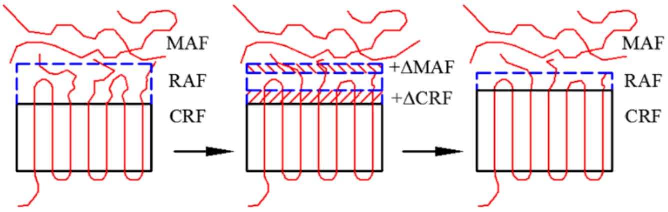


Figure 4. *RAF-CRF and RAF-MAF rearrangement during the post-crystallization process*

Conclusion

Based on the results it can be concluded that significant changes of morphological and mechanical properties of recycled PET are caused by technological parameters, not by the IV (intrinsic viscosity – depends on molecular weight) value of regranulates. Understanding changes of morphology of injection molded samples and finding the correlation between the structure and the mechanical properties, and their change as a function of time elapsed after production can help us to control the properties of injection molded samples.

2.2. Upgrading recycling of PET waste by the development of flame retarded nanocomposites of reduced additive contents

Recycled PET products with improved fire resistance and adequate mechanical properties would be suitable for applications in the electronic field. The flame retardancy of PET is, however, rather challenging due to its low melt strength and to the required high processing temperature. In this work, among the environmentally friendly, non-halogenated flame retardants an aluminium-phosphinate (AlP) based additive was chosen as base flame retardant agent. In order to improve its effectivity without noticeably increasing the needed additive content, a wide series of nanoadditives were tested as potential synergists. The flammability characteristics of the test samples were investigated together with the rheological and mechanical properties in all cases.

Screening of potential nanosynergists

First, the flame retarding effect of 6 types of nanoparticles, talc, TiO_2, Na-MMT, Fe-MMT, hydrophilic SiO_2 and hydrophobic SiO_2 were tested at 1 wt% besides 5 wt% of AlP. The UL94 ratings and the measured LOI values of the obtained samples are presented in ***Table 1***, and the evaluated experimental data recorded during mass loss type cone calorimetric measurements are shown in ***Table 2***.

	LOI (vol%)	**UL94 (rating)**
O-PET	23	V-2
O-PET+5%AlP	29	V-0
O-PET+5%AlP+1%talc	30	V-0
O-PET+5%AlP+1%TiO_2	33	V-0
O-PET+5%AlP+1%Na-MMT	31	V-0
O-PET+5%AlP+1%Fe-MMT	30	V-0
O-PET+5%AlP+1%hydrophilicSiO_2	31	V-2
O-PET+5%AlP+1%hydrophobicSiO_2	30	V-2

Table 1. *Result of Limiting Oxygen Index and UL94 test (specimens based on original PET)*

	TTI (s)	**pkHRR** (kW/m^2)	**pkHRR$_{time}$** (s)	**Residue** (%)	**THR** (MJ)
O-PET	192	197	226	13,2	7,9
O-PET+5%AlP	213	158	248	11,7	9,5
O-PET+5%AlP+1%talc	195	144	214	15,5	6,8
O-PET+5%AlP+1%TiO_2	212	160	249	11,9	8,1
O-PET+5%AlP+1%Na-MMT	195	136	218	13,8	6,9
O-PET+5%AlP+1%Fe-MMT	248	171	224	13,3	8,3
O-PET+5%AlP+1%hydrophobicSiO_2	203	147	241	14,5	9,4
O-PET+5%AlP+1%hydrophilicSiO_2	180	170	219	11,0	8,4

Table 2. *Result of Cone Calorimetry test (specimens based on original PET)*

When considering the results of all the three flammability tests (***Table 1 and 2***) the Na-MMT proved to be the best synergist. With the combined application of AlP and Na-MMT the best V-0 rating according to the standard UL94 test and a LOI value as high as 31 vol% were reached and a 30% reduction of the peak of heat release rate was achieved.

The notched Izod impact strength (‘a’) of the prepared samples was also evaluated. It can be seen in ***Figure 5*** that the addition of AlP causes significant reduction of the impact strength and consequently all the prepared flame retarded compositions have only moderate impact resistance. To diminish the thermal and hydrolytic degradation during reprocessing proved to be a key issue to obtain flame retarded samples with adequate mechanical properties. Therefore, comprehensive experiments were carried out to optimize the technological parameters of sample preparation, i.e. drying, extrusion and injection moulding.

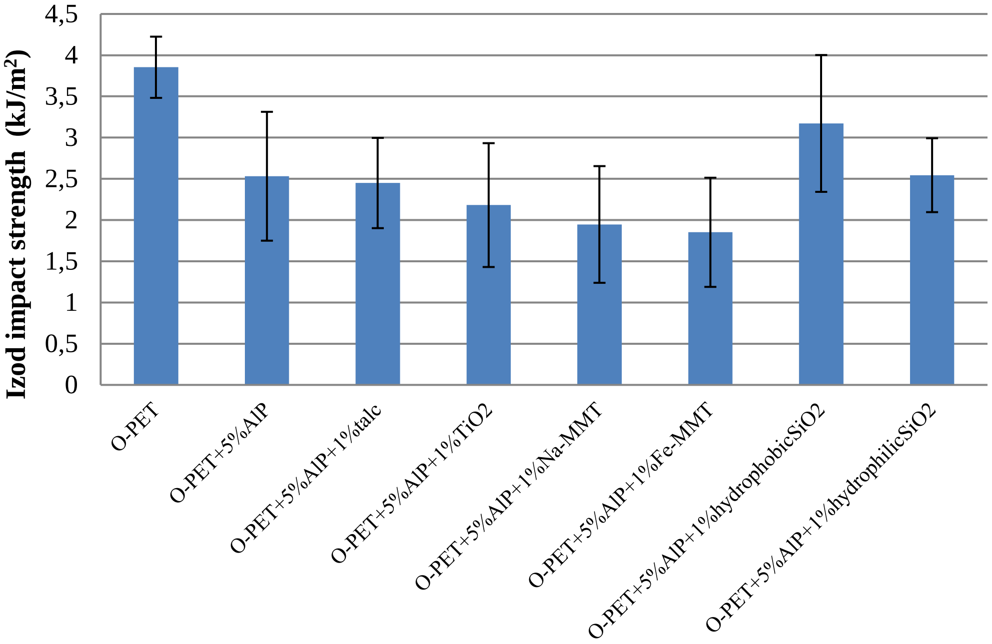


Figure 5. *Notched Izod impact strength of samples based original PET*

Preparation and characterisation of flame retarded recycled PET samples

As a next step, the composition of the AlP and Na-MMT containing samples was optimized (Main investigated properties: flammability (UL rating) and impact strength).
Tested concentrations: AlP + Na-MMT: 4+0; 4+0,7; 4+1; 5+0; 5+0,7 and 5+1. Flame retarded samples were manufactured from the PET waste with the optimized composition (5% AlP + 1% Na-MMT). As electronic applications are targeted, also the effect of black dye (BD) was investigated.

The flammability characteristics of the obtained recycled PET (R-PET) samples were characterized by UL94 tests, LOI measurements and cone calorimetry. The UL94 ratings and the LOI values are summarized in ***Table 3***, and the heat release rate curves are shown in ***Figure 6***.

	LOI (vol%)	UL94 (rating)
R-PET	24	V-2
R-PET+5%AlP	29,5	V-0
R-PET+5%AlP+1%Na-MMT	31	V-0
R-PET+5%AlP+1%Na-MMT+1%BD	29,5	V-0

Table 3. *Result of Limiting Oxygen Index and UL94 test (specimens based on recycled PET)*

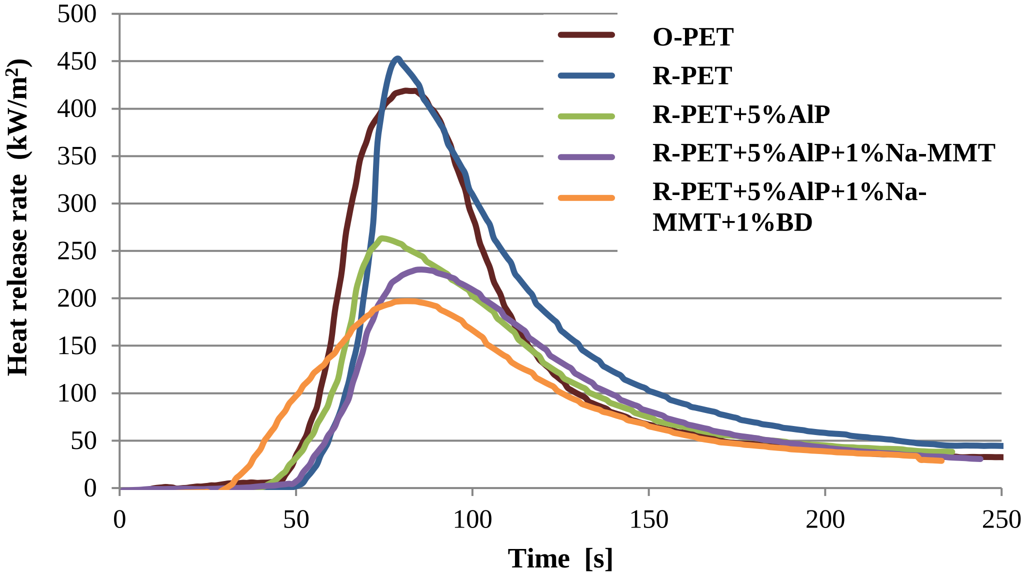


Figure 6. *Results of Cone-calorimetry investigation*

When comparing the results of ***Table 1 and 3***, it can be seen that the flame retarded R-PET samples have just as high LOI values as the original counterparts. Nevertheless, the addition of 1% black dye slightly reduces the LOI, the UL94 V-0 rating could be still ensured in this case. When considering the heat release rate curves (***Figure 6***) it can be seen that significantly less heat is released during the combustion of the optimized recycled sample (R-PET+5%AlP+1%Na-MMT+1%BD) than in the case of the additive-free references (O-PET and R-PET), a 55% reduction of the pkHRR was achieved.

The impact resistance of the recycled samples was tested as well. As it is shown in ***Figure 7***, thanks to the optimized composition and processing parameters significant property damage cannot be observed anymore, the flame retarded recycled PET has just as high impact resistance as the additive-free primary PET (O-PET).

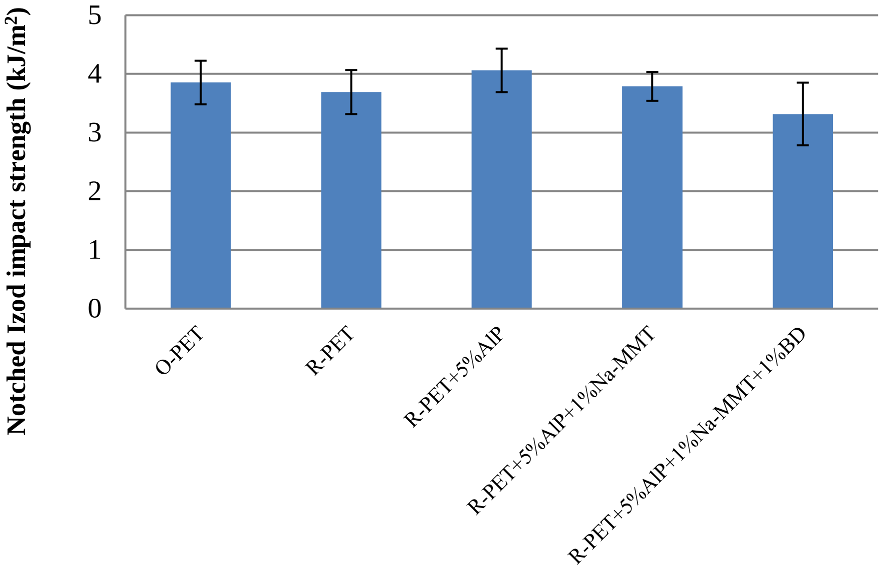


Figure 7. *Notched Izod impact strength of samples based recycled PET*

Based on the developed formulation, glass fiber reinforced material was prepared and tested as well. The used chopped glass fiber (3B Company) could increase effectively not only the tensile strength and the stiffness but also the impact strength of the flame retardant material (***Figure 8.***)

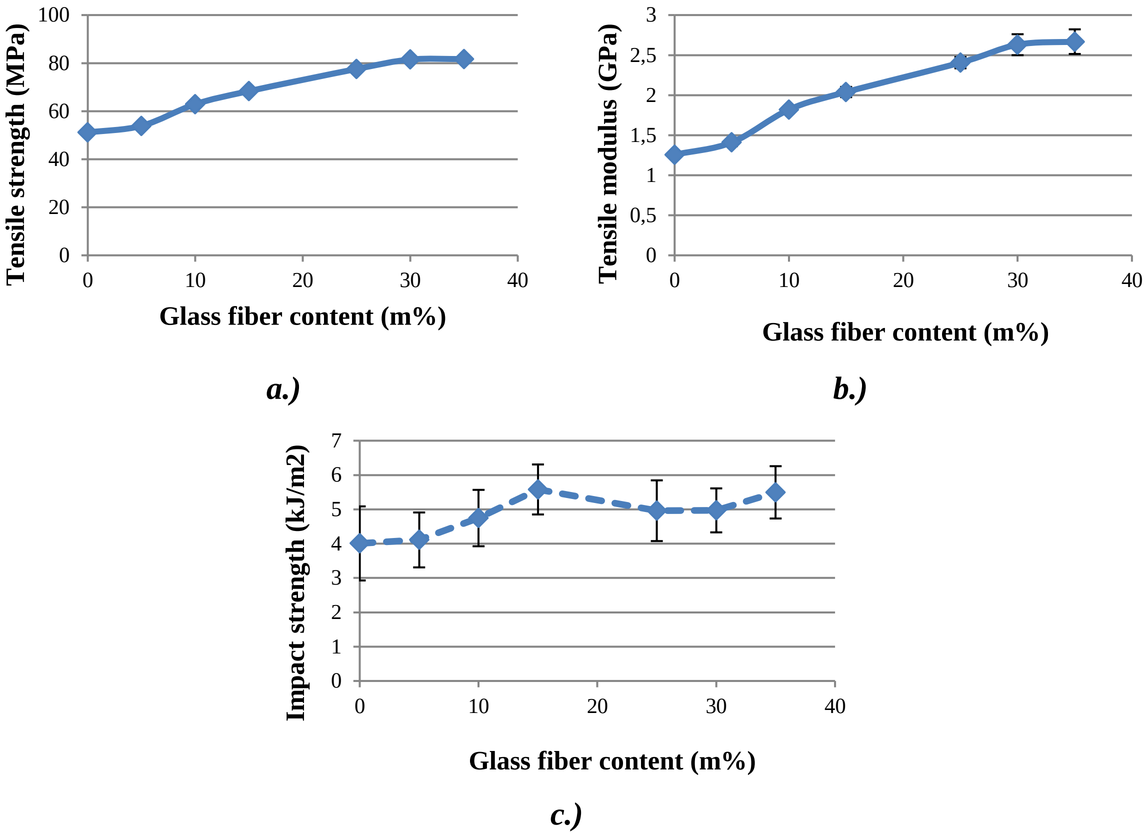


Figure 8. *Tensile strength (a.); tensile modulus (b); and Izod impact strength (c) of fiber reinforced, flame retardant PET*

Glass fiber content had negative effect on flammability (***Table 4***), UL94 rating of the glass fiber reinforced specimens were V2.

Glass fiber + AlP + Na-MMT	*UL94 rating*
0+5+1	*V0*
5+1+1	*V2*
10+5+1	*V2*
15+5+1	*V2*
25+5+1	*V2*
30+5+1	*V2*
35+5+1	*V2*

Table 4. *UL94 test (specimens based on glass fiber reinforced PET)*

Conclusion

Flame retarded nanocomposites with prominent fire resistance and adequate mechanical properties were developed using secondary PET as raw material. By utilizing the synergism between aluminium-phosphinates and nanoclays, self-extinguishing behaviour (i.e. UL94 V-0 rating), LOI as high as 29,5 vol% and significantly reduced heat emission during combustion were achieved by using only 6 wt% additives. Due to the low additive content and the optimized processing parameters the impact resistance of the recycled material reaches that of the original additive-free PET. It is presumed that the developed recycled material, based on its improved flame retardant properties and low cost could become especially attractive for the industry.

2.3. Development of closed-cell PET foams

Foaming is a common procedure in the plastic industry. It can be a separate technology (e.g. manufacturing EPS foam), or part of another manufacturing process (e.g. injection moulding, extrusion). There are also various classifications (according to foam structure, density or manufacturing procedure). The procedures can be classified into two groups according to manufacturing process:

- physical: two types are possible
  - gas is blown into the melt or
  - a foaming agent of low boiling point is added, which creates the foaming gas through a change of state;
- chemical: the foaming gas is produced with a chemical reaction

During research chemical (via extrusion and injection moulding) and physical methods (via extrusion) were investigated in order to achieve PET foam with reduced density from recycled material.

Chemical foaming

Extrusion with Chemical Blowing Agents (CBA)

Extrusion mold was designed and manufactured in order to produce sheet with cross-section high enough for foaming (***Figure 9***).

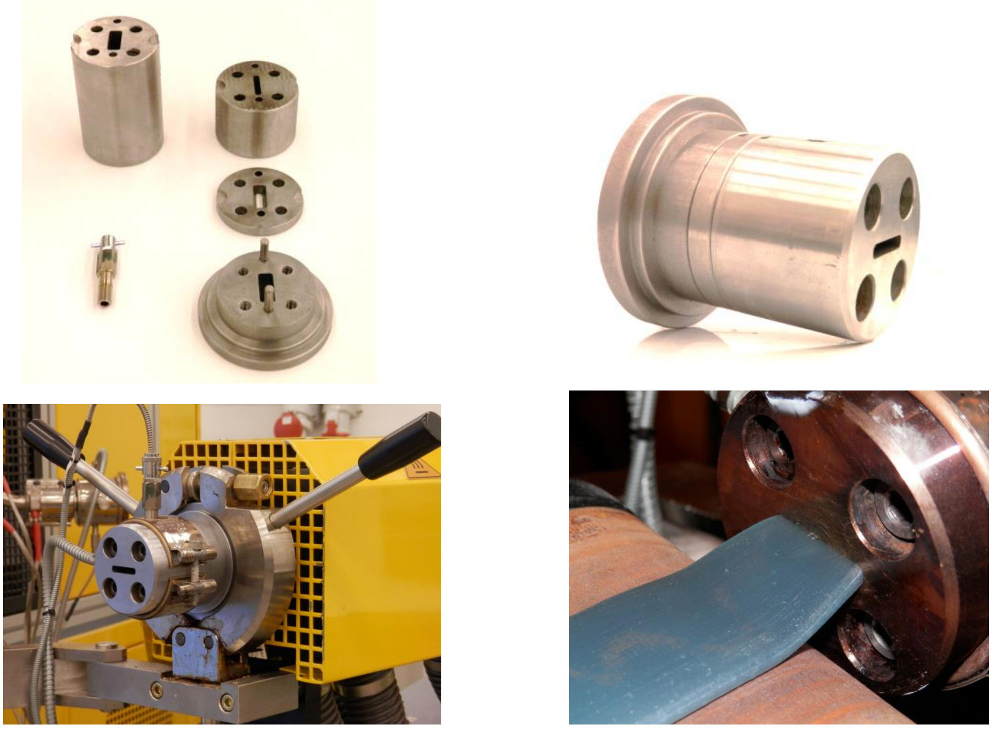


Figure 9. *Manufactured modular extrusion mould before and during recycled PET extrusion*

Samples were made with 0, 2, 4 and 6 m% foaming agents. Based on the results the best composition was: 88.3 m% recycled PET, 2m% Chain extender, 4.5m% AlP flame retardant additive, 1.2% NaMMT and 4% foaming agent (***Figure 10***).

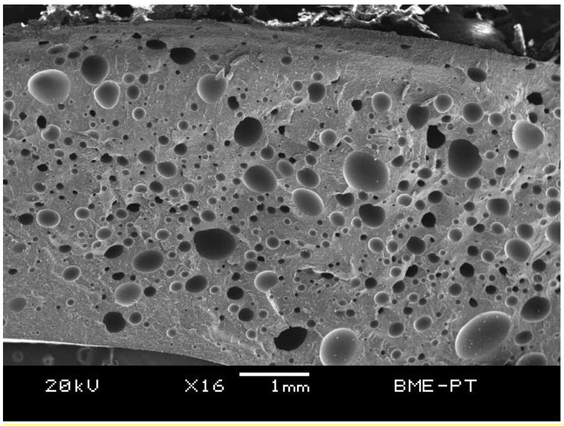


Figure 10. *SEM image of flame retardant, foamed sheet*

Based on morphological and flammability tests it can be concluded, that density of the sheet decreased significantly however the flame retardant properties slightly deteriorated.

Injection moulding with Chemical Blowing Agents (CBA)

In this step thick-walled products were injection molded from recycled PET using exothermic and endothermic chemical foaming agents. Foam structure and morphological properties of the prepared samples and the impact of mold temperature on the properties were examined.

Different foam structures were formed in the samples due to the two kinds of foaming agents. When endothermic foaming agent was applied, finer foam structure formed along the cross section with smaller cell size, while the density of products decreased by 29%. In case of exothermic foaming agent a coarser structure with larger cell size formed, and the density decreased by 14%. Although exothermic foaming agent develops more gas during its decomposition than the endothermic one, but due to the smaller melt viscosity and higher pressure gas cells approach the surface of the product and a part of the gas may even leave the product.

Porosity of samples showed strong relationship with mold temperature. As mold temperature increased the porosity of samples with endothermic foaming agent decreased, and that of samples with exothermic foaming agent increased. In case of endothermic foaming agent, the gas cells formed are smaller and there is an increasing number of cells as the middle of the sample is approached, while in case of exothermic foaming agent a more porous layer can be found both in the edge and middle of the samples (***Figure 11***).

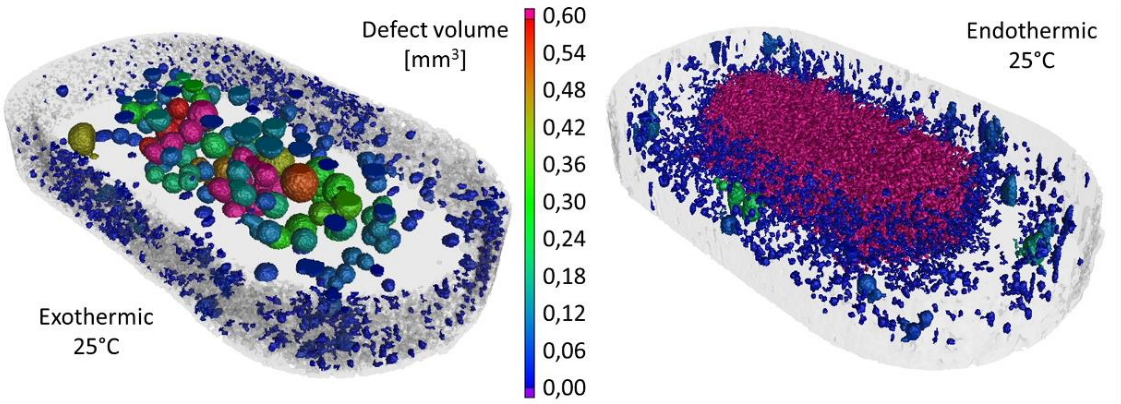


Figure 11. *Cell size based on CT images in case of exothermic and endothermic foaming agents*

Crystalline structure of RPET and samples prepared with different foaming agents showed significant differences. The crystalline ratio of samples with foaming agent changed significantly compared to samples with no foaming agent. The crystalline ratio of samples with exothermic foaming agent increased, while that of samples with endothermic foaming agent decreased. The reason is the melt temperature difference and therefore the different cooling rate and time. RAF was smaller in case of foamed samples, while MAF was larger compared to that of the sample made of the original material. The reason is the different size and number of crystallites, and therefore their different surface-volume ratio.

Based on the results high density foams and thick-walled products can be produced if recycled PET is chemically foamed. Development and manufacture of foamed products may open new fields in PET recycling.

Physical foaming (extrusion using supercritical CO_2)

The goal of the investigation was to produce r-PET foam by using supercritical CO_2 as a blowing agent. To produce mechanically stable r-PET foam, on the one hand we had to increase its average molecular weight (MW) and crystallization rate (CR%) with different additives, like using chain extenders and nucleating agent, on the second hand we had definite the right extrusion process parameters as well.

Based on pre-research, we investigated on 3 chain extenders (CE) and 2 nucleating agents to attempt to reach our goal. ***Table 5.*** includes the used additives' names, sources and forms.

Additives		
Chain extenders (CE)	Epoxi based (master batch): **Epoxi 1**.: (Gabriel-Chemie PET795000EXT) **Epoxi 2**.: (Clariant Cesa EXT)	Di-anhidrid based (powder): **(di)anhirdid:** (Sigma Aldrich, PMDA EXT)
Nucleating agents	Montmorillonite (15μm)	Talc (1μm)

Table 5. *Used additives*

Step 1: Chain Extenders

According to the results (***Figure 12.***), the (di)anhidrid CE increases the average MW of the r –PET the most, using the less amount of it at the same time. Only comparing the Epoxi 1 to Epoxi 2, there isn't significant difference regarding to their chain extension effect. Although, the (di)anhidrid CE has the largest effect, but the production was not steady state due to the powder form of (di)anhidrid. At the case of Epoxi 1, it was same related to the extrusion process. As a consequence of these facts, the Epoxi 2 was used for the further investigation.

Based on Berkowitz (1) equation, the measured Intrinsic Viscosity (IV) ('η') values were transferred to (average) MW values.

$$M_w = 6.58 \text{ x } \eta^{1.54} \quad (1)$$

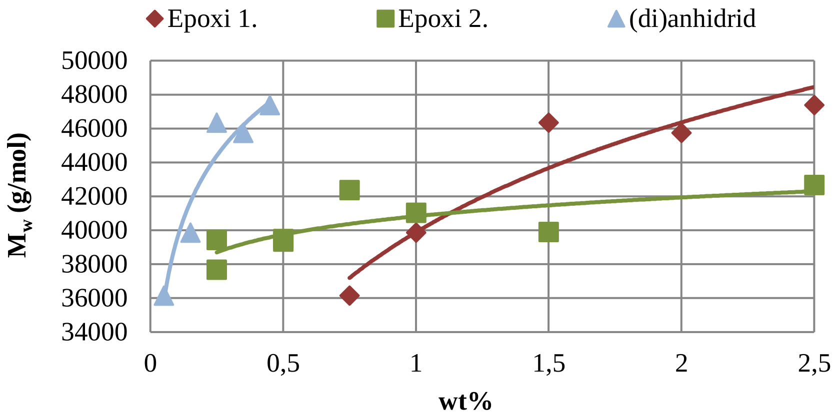


Figure 12. *Chain extenders' effect on MW of r-PET*

Step 2: Nucleating Agents (NA)

Basically, nucleating agents are used in polymer technology to increase the crystallite rate in polymers. Their biggest importance resides in the particle size. The practical size has influence not just to the crystallite rate, but to the intrinsic viscosity as well. Generally, NAs has effect on the mechanical properties of the polymers. At this case we used two different types for r-PET, Na-MMT (15µm) and talc (1µm).

Based on investigations the lower the size is, the higher the CR%. However, the results showed, there is no significantly deviation related to the CR% (***Figure 13.***), due to there is not a big size difference. Another point of view, the bigger particle size caused lower intrinsic viscosity (***Figure 14***). Briefly, it is most beneficial by using talc.

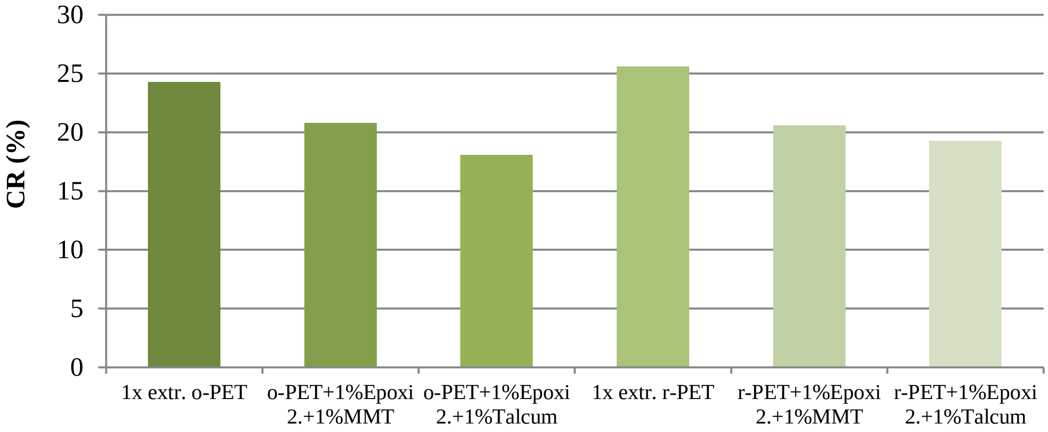


Figure 13. Effect of nucleating agents on CR% of r-PET

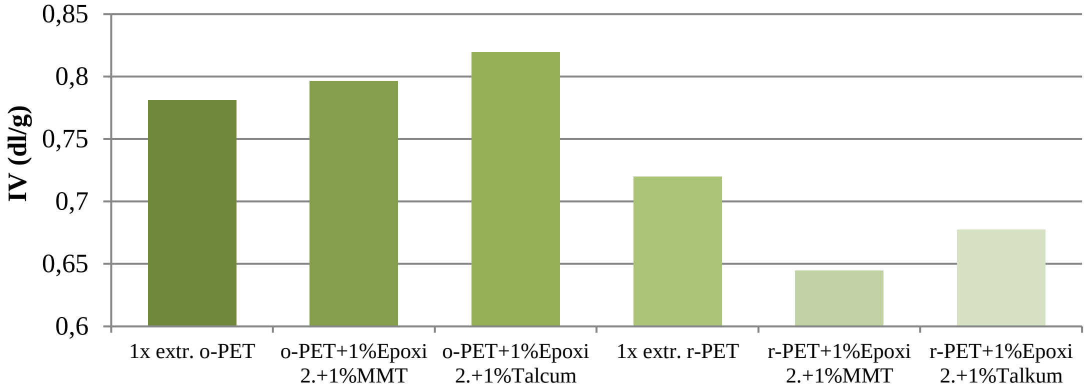


Figure 14. Effect of nucleating agents on IV of o–PET and r-PET

Step 3: Foaming process

During the foaming process 5 different material compositions were used (***Table 6***). Investigation was made on recycled PET (r-PET), original PET (o-PET), and PET with high IV (PET (0,86 IV)).

The optimal process parameters (***Table 7.***) were determined by using previous studies related to this topic and by using our experiences.

	Composition		
	Main component	**Additives**	
		Chain extender (wt%)	**Nucleating agent (wt%)**
1. production	r -PET	2% Epoxi 2.	2% Talcum (1μm)
2. production	r -PET	2% Epoxi 2.	1% Talcum (1μm)**
	o -PET	1% Epoxi 2.	1% MMT (15μm)**
3. production	o -PET *	1% Epoxi 2.	1% Talcum (1μm)
4. production	PET (0,86 IV)	1% Epoxi 2.	1% Talcum (1μm)

* All components were added during the foaming process, there was not pre-extrusion.

** Different die formation (pipe shape)

Table 6. *Used material compositions for the foaming process*

Process parameters	**Main component**	
	o –PET & PET(0,86 IV)	**r-PET**
Drying (time, temperature)	4h, 140°C	
Extrusion process temperature profile	250-265-260-270-175-140 °C	244-255-220-225-220 °C
Screw speed	20-40 rpm	
Die pressure	71 bar	24 bar
Motor torque	57%	67%
sc.CO_2 Flow	1 ml/min (65-70 bar)	0,6 ml/min (76-83-97,6 bar)
Melt temperature: T_m	206/204 °C	224 °C

Table 7*. Parameters of the foaming process*

Characterization of extruded PET foam

In ***Figure 15.*** the density and IV values of foams are compared to each other. Foam density was the lowest at the case of 5. foam, when r-PET was the main component (+2%Epoxi 2+1%Talcum). From IV point of view the 1. foam has the highest values, but that followed by 2. and 5. foams. Bases on the measurements, r-PET is suitable for producing low density foams, thanks to the chain extension and the increased crystallite rate.

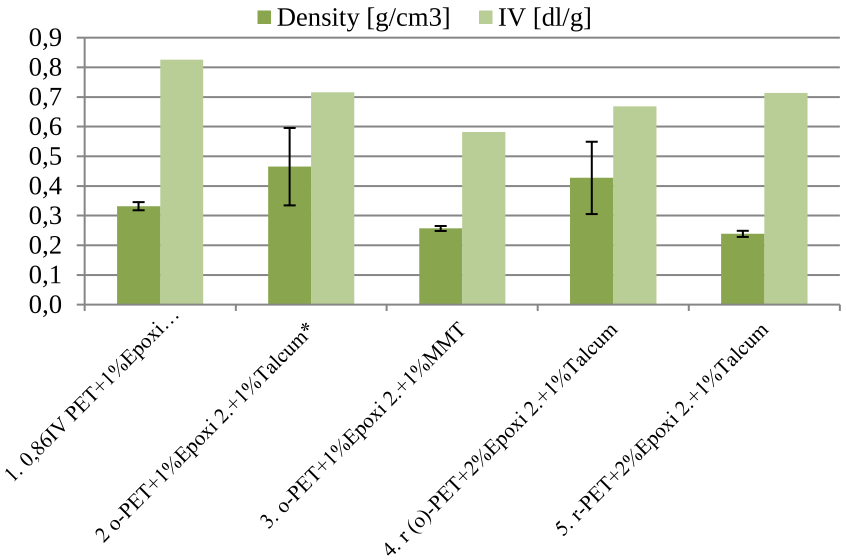


Figure 15. *Density and IV values of the produced foams*

Cell size and cell density

In ***Table 8***. the foam properties are summarized shortly based on the SEM pictures, what can be seen below the table.

Nr.	**1.**	**2.**	**3.**	**4.**	**5.**
	0,86IV PET+ 1%Epoxi 2.+ 1%Talc	**o-PET+ 1%Epoxi 2.+ 1%Talc**	**o-PET+ 1%Epoxi 2.+ 1%MMT**	**r-PET+ 2%Epoxi 2.+ 1%Talc**	**r-PET+ 2%Epoxi 2. + 1%Talc**
Cell size	~ 700-1000μm	~ 100-400μm	~ 20-100μm	~ 80-150μm	~ 200μm
Disper-sion	homogeneous	heterogeneous, because a different die formation was used,	heterogeneous, because a different die formation was used	homogeneous	homogeneous
Figure	***16.***	***17.***	***18.***	***19.***	***20.***

Table 8. *Results of morphological investigation*

At every case, we could produce lower density and microcell size foams. However, the 1. and the 5. production resulted homogenous foam and stable process. Comparing the 1. to the 5. production the cell size was similar, but the wall thickness of the 5. production was thinner and its cells were more stable due to the higher MW of PET. At the other three cases, the productions were not efficient, but they were useful attempts to gain more experience about material compositions and process methods.

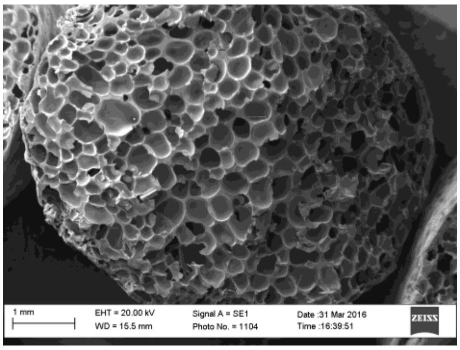


Figure 16. *PET (0.86 IV) +1% Epoxi 2. +1% talc*

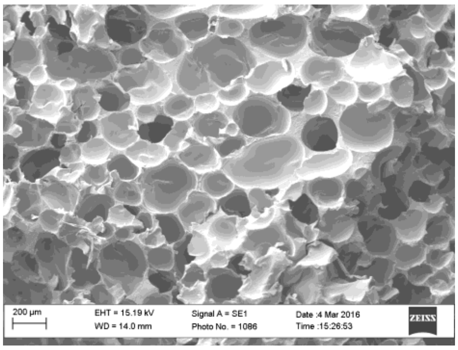


Figure 17. *o-PET+1% Epoxi 2. +1% talc*

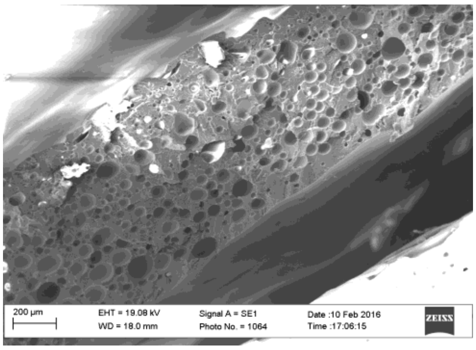


Figure 18. *r-PET +1% Epoxi 2. +1%MMT*

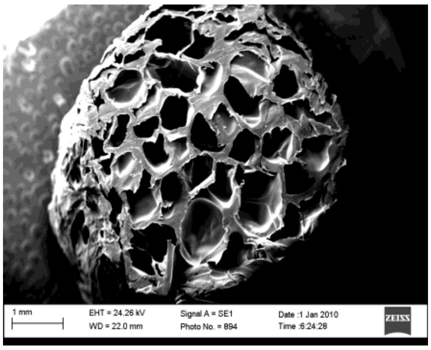


Figure 19. *r-PET+2% Epoxi 2.+1% talc*

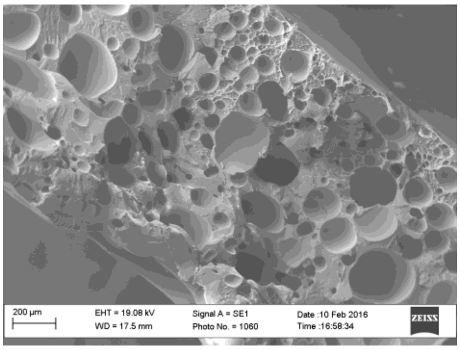


Figure 20. *r-PET +2%Epoxi 2. +1% talc*

Summary

According to the experiments, low density, microcell foams from recycled PET can be produced by using chain extender and nucleating agents.

2.4. Investigation of polymer blends based on PET

In this chapter the rheology, change of morphology and the mechanical properties of PET/HDPE blends with and without SEBS-g-MA additive were investigated. The results of rheological investigations show that SEBS-g-MA acts differently on the components: viscosity of PET was higher in a way that the difference was the same at every shear rate if it contained SEBS-g-MA; but the viscosity of HDPE that contain SEBS-g-MA changed differently than that of HDPE without the additive in the range where our measurements were carried out. The viscosity ratio of PET/HDPE blends changed differently depending on the presence of SEBS-g-MA, and that had an effect on the morphology of the blend.

In PET/HDPE blends produced by extrusion a fibrous structure was formed in the direction of the shear flow, in contrast to injection moulded samples where shell / core morphology could be observed. In case of extrusion phase inversion occurred at 30 vol% PET, while injection moulded samples showed a wider range of co-continuous structure (30 to 40 vol% PET) in PET/HDPE blends. The morphological studies show that co-continuous structure was also formed in an asymmetric composition because of the high viscosity of HDPE at 275°C, and that proves that not only the content ratio, but also the viscosity ratio of the components has a significant effect on the morphology developed. Therefore, co-continuous morphology was immediately formed when PET reached the required proportion, i.e. 30 vol%. When SEBS-g-MA was added to the PET/HDPE blends, the additive widened the range of phase inversion of the blends, especially in case of extrusion (***Figure 21***).

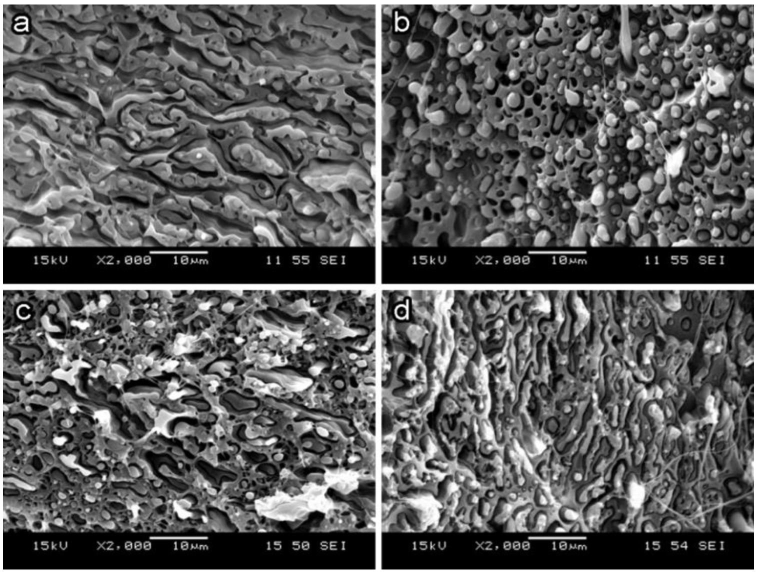
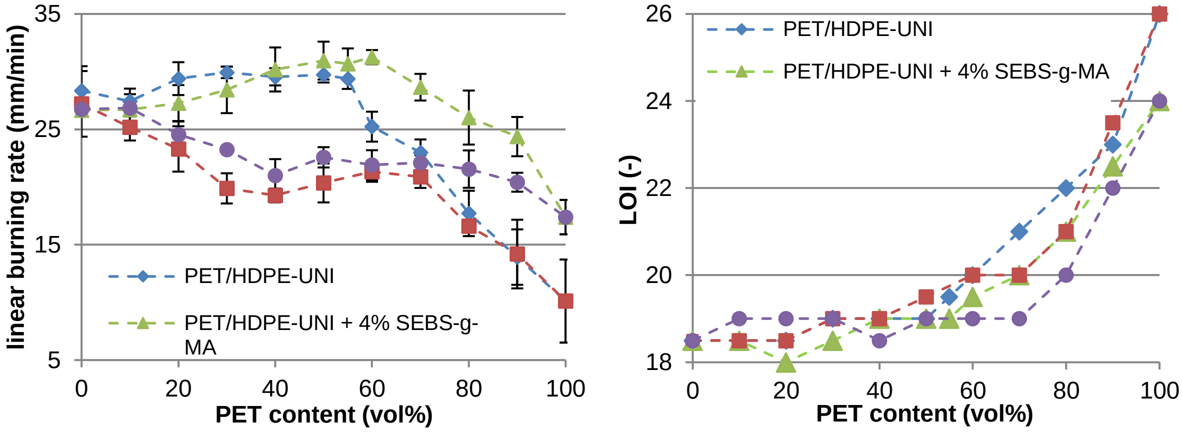


Figure 21. *Fracture surface of PET/HDPE blends, (after extrusion), with a composition-ratio of: (a) 30/70; (b) 40/60; (c) 30/70 + 4 vol% SEBS-g-MA; (d) 40/60 + 4 vol% SEBS-g-MA*

The results of mechanical tests revealed that SEBS-g-MA slightly decreases the tensile strength and the Young's modulus of PET/HDPE blends; while elongation at break improved in cases when the breakage took place under 100% elongation because of the toughening effect of SEBS-g-MA on the PET/HDPE blends.

The influence of the morphology and compatibilizer on burning behavior of PET/HDPE blend has been presented as well (***Figure 22***). Due to the different viscosity ratio, the phase inversion occurred under different composition in blends. The co-continuous morphology formed at 55-60 vol% PET in blend consists of HDPE with higher flow rate (referred as HDPE-UNI), while blending the lower flowability HDPE (referred as HDPE-TVK) to PET, 30-40 vol% PET was enough to reach the phase inversion. The presence of SEBS-g-MA compatibilizer in PET had no effect on thermal stability, while it had a slight reducing influence when introduced to HDPE.



(a) (b)

Figure 22. *(a) Linear burning rate and (b) LOI of blends, shown with the following symbols: (♦) PET/HDPE-UNI, (▲) PET/HDPE-UNI + 4% SEBS-g-MA, (■) PET/HDPE-TVK and (●) PET/HDPE-TVK + 4% SEBS-g-MA*

Comparing the burning rate of PET/HDPE blends, it can be stated that burning was faster with greater flammability when the matrix was formed by HDPE. Consistent results have been achieved in LOI studies, there was no significant change in LOI values in case of blends where HDPE showed continuous structure. Nevertheless, after phase inversion LOI was greatly increased. The negative impact of SEBS-g-MA was also appearing in blends. PET/HDPE blends with compatibilizer showed higher burning rate in most case, the difference was particularly significant after phase inversion.

2.5. Alternative polymer separation technology by centrifugal force in a melted state

In order to upgrade polymer waste during recycling, separation should take place at high purity. In the research a novel, alternative separation technology was developed, where the polymer fractions were separated by centrifugal force in melted state (***Figure 23***). The efficiency of the constructed separation equipment was verified by two immiscible plastics (polyethylene terephthalate, PET; low density polyethylene, LDPE), which have a high difference of density, and of which large quantities can also be found in the municipal solid waste.

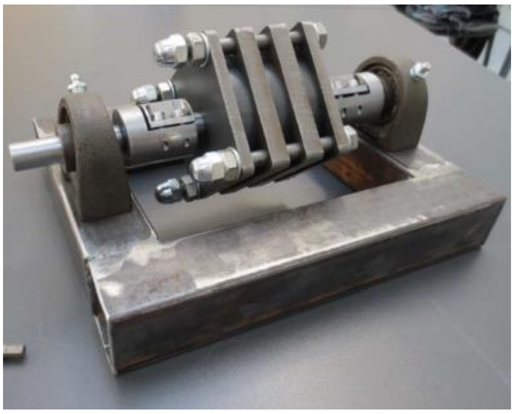


Figure 23. *The developed prototype of polymer-separator*

The results show that the developed equipment is suitable not only for separating dry blended mixtures of PET/LDPE into pure components again, but also for prefabricated polymer blends. Hence, this was the first time it was possible to separate two different plastics into neat fractions in a melted state with the developed equipment. This polymer blend separation process is completely different, faster and more environmentally friendly technology than using solvent agents. With this process it may become possible, during the recycling process, to recover the pure polymer substances from products, which were manufactured from several polymer substances at the same time (***Figure 24***).

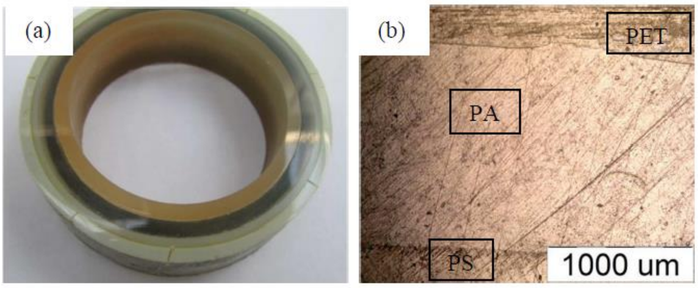


Figure 24. *(a) Separated PET, PA, PS and PP zone, from the outer layers respectively; (b) boundary between pet6pa6ps zones /optical microscope image/*

Compared to the currently used technologies, this method is more economical, time efficient and last but not least, it is more precise, as it concludes to the composition of the waste stream by analyzing larger fractions of it.

Preparing polymer blends is an effective way to tailor the good properties of plastics but the most commonly used polymers are incompatible with each other. Therefore, to reduce the interfacial tension and to achieve finer and stable morphology, a suitable copolymer or compatibilizer has to be added to blends in order to establish new interactions between the phases. However, it is difficult to determine the required amount of compatibilizers in polymer blends. As an outcome of the present research a novel separation method was developed, where the blends are investigated in melted state, utilizing centrifugal force to determine the adequacy of compatibilizers.

During the process the compounded 50/50 vol% PS/HDPE blends were the same as in other investigations, produced with a twin screw extruder. The adequacy of compatibilizers have been investigated in blends with different SEBS-g-MA content (0-10 vol%). The separation occurred in melted state, utilizing centrifugal force. Owing to the influence of centrifugal force, the melted PS droplets, which can be characterized with higher density than HDPE, can migrate towards the wall of the separation tank, while HDPE phases move towards the shaft during the spinning phase of the separation process. The separation process can result in three different types of zones as parts of the separated disc: a pure outer zone of PS, a pure inner zone of HDPE and a potential transition zone, wherein the two plastics and compatibilizer SEBS-g-MA can also be found at the same time. The thickness of the formed zones can be measured by optical microscopy, after the discs are polished. In case the PS/HDPE blend did not contain compatibilizer, the melted phases solidified during shape-fixing and formed two separated, pure zones in the disc with a sharp transition boundary, i.e. the outer zone contained only PS and only HDPE was located in the inner zone (***Figure 25***). Conversely, when 0.5% SEBS-g-MA was added to PS/HDPE blend a large transient, compatibilized zone formed between the neat HDPE and neat PS zone

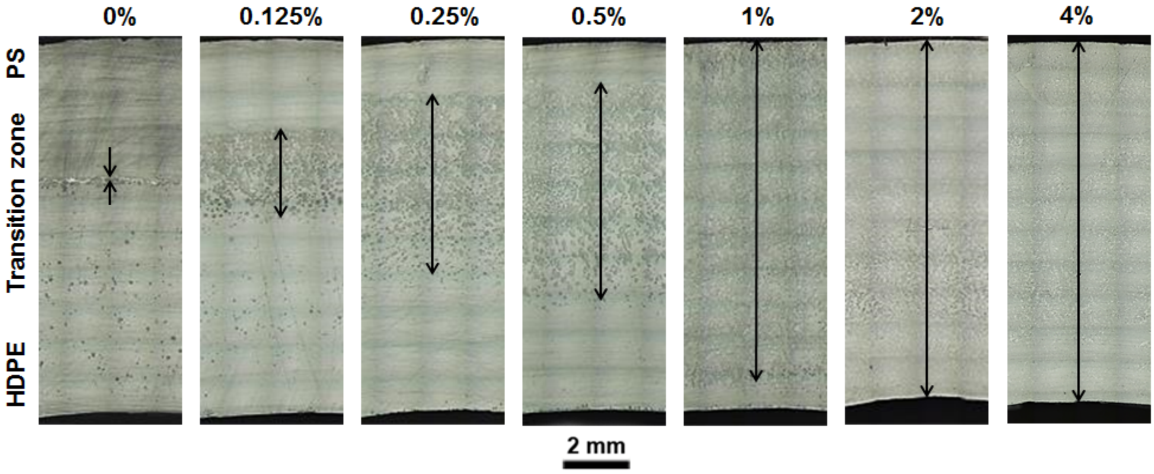


Figure 25. *Thickness of compatibilized transition zone /with different compatibilizer content/*

The results lead to the conclusion that the novel separation method, where the blends are investigated in melted state, and that uses centrifugal force can be suitable for predicting the adequacy of compatibilizer in polymer blends.

3. Summary

3.1. New scientific thesis based on research project

1st thesis

Significant changes of morphological and mechanical properties of recycled PET are caused by technological parameters, not by the IV value (intrinsic viscosity – depends on molecular weight) of regranulates. Understanding changes of morphology of injection molded samples and finding the correlation between the structure and the mechanical properties, and their change as a function of time elapsed after production can help us to control the properties of injection molded samples.

2nd thesis

Flame retarded nanocomposites with prominent fire resistance and adequate mechanical properties were developed using secondary PET as raw material. By utilizing the synergism between aluminium-phosphinates and nanoclays, self-extinguishing behaviour (i.e. UL94 V-0 rating), LOI as high as 29,5 vol% and significantly reduced heat emission during combustion were achieved by using only 6 wt% additives.

3rd thesis

Low density, microcell foams from recycled PET was produced by using supercritical CO_2. In order to achiave optimized cell-structure chain extender and nucleating agents are needed. Composition of flame retardant, foamed recycled PET was developed as well, using chemical foaming agents and nanosized synergic agents.

4th thesis

The range of phase inversion of an immiscible polymer blend can be detected indirectly with measuring the mould-shrinkage of injection moulded specimens or determining the limiting oxygen index of blends. Increasing the volume ratio of the phase characzerized by smaller shrinkage increasingly reduces the shrinkage of blends. In contrast, when the component with greater shrinkage is the dispersed phase has no effect on the shrinkage of blend and the values of the shrinkage depends only from the continuous phase due to the weak adhesion between the phases. The less flammable component has no influence on the limiting oxygen index until it is located as dispersed phase in the more flammable matrix structure. The claim was justified by the results of PET/HDPE blends.

5th thesis

The presence of compatibilizer has significant influence not only on mechanical properties but also on the burning characteristics of immiscible polymer blends. Adding 4 vol% of SEBS-g-MA to PET/HDPE blends resulted in at least two times higher elongation and at least 40% higher Charpy impact strength because of improved adhesion between the phases comparing blends with the same composition ratio without additive. At the same time the compatibilizer reduces the tensile moduli of blends in the whole range of the measurement; furthermore the resistance to burning decreases in PET/HDPE blends, when morphology was co-continuous or dispersed structure where the matrix is constituted by the less flammable PET.

Due to the highly flammable SEBS-g-MA additive forms combustion hotspots in the continuous PET phase leads to the burning rate of these blends significant increase at as it decrease the values of limiting oxygen index.

6th thesis

Two or more immiscible polymers can be separated from each other at high purity and the composition ratio of the identified polymers can be analyzed with a novel density difference-based principle, where the enrichment process occurred in a melted state of the polymers utilizing centrifugal force. For the successful separation at least 0,05 g/cm^3 density difference is necessarry between the phases measured by the applied separation temperature in melt state and the proportion of component can vary from 5 to 95 vol% in the mixture.

The microstructure of blends, where the phases were previously homogenizated by compundation can be decomposed without using chemical solvents with the developed centrifuge separator, in which the separation occurred in a melted state of the polymers.

With the novel evaluation method based on separation, where the blends are investigated in melted state utilizing centrifugal force can be suitable for predicting the adequacy of compatibilizer in polymer blends and to estimate the minimum required amount of compatibilizer, which causes a significant change in the property of blend.

3.2. Additional education/research results

Education activity connected to research project

Scientific Students' Associations activity (SSA)

1. Domán Júlia: Reciklált PET értéknövelő újrahasznosítása égésgátolt nanokompozitok fejlesztésével, 2016, előadásra elfogadva
2. Kovács Bálint Máté: Polisztirol és polietilén keverékek tulajdonságainak vizsgálata és elemzése, 2015 TDK dicséret
3. Horváth Ádám: Polimerömledékek szétválaszthatóságának vizsgálata és elemzése centrifugális erőtérben, 2015 **TDK 1. díj**
4. Budinszki Balázs: Kompatibilizálószerek újfajta minősítése centrifugális erőtérben, 2014 **TDK 1. díj**, OTDK III. díj
5. Szabó Diána Katalin: Természetes és mesterséges polimerek ömledékállapotban történő szétválaszthatósága, 2014 TDK 2. díj, **OTDK I. díj**
6. Iván Georgina, Gere Dániel: PET degradációjának nyomon követése az újrahasznosítás során, 2014 TDK 1. díj, **OTDK különdíj**
7. Molnár Ádám: Kompatibilizálószer hatása PET/HDPE keverékekben, 2013 TDK 3. díj
8. Szilágyi László: Feldolgozási paraméterek hatása háromfázisú polimer keverékek morfológiai és mechanikai tulajdonságaira, 2013 **TDK 2. díj, Bodor Géza** különdíj
9. Csergő Vencel: Szétválasztó ömledékcentrifuga tervezése és minősítése autóipari műanyaghulladék vizsgálata céljából, 2013 TDK dicséret

BSc final project

Budapest University of Technology and Economics:

1. Szabó Olivér: Reciklált polietilén-tereftalát felhasználása ömledékrétegzés alapú (FDM) additív gyártástechnológiához, 2016 - folyamatban
2. Mudriczki Péter: Összetétel-arány hatása polimer keverékek reológiai-, morfológiai- és mechanikai tulajdonságaira, 2015
3. Horváth Ádám: Polimerek ömledékállapotú szétválaszthatósága és degradációs hatásai, 2015
4. Kovács Bálint Máté: Az összetétel-arány és a feldolgozási paraméterek hatása polimer keverék reológiai, morfológiai és mechanikai tulajdonságaira, 2015
5. Budinszki Balázs: Kompatibilizálószer hatása polimer keverékek mechanikai tulajdonságaira és szétválaszthatóságára, 2014

1. Paizs Ákos: Műanyagok szétválaszthatóságának vizsgálata ömledékállapotban, 2014
2. Bonnyai Bence: Polimerek fizikai habosíthatóságának vizsgálata, 2014
3. Gere Dániel: Az újrafeldolgozás során alkalmazott paraméterek hatása a PET morfológiai és reológiai tulajdonságaira, 2014
4. Iván Georgina: PET anyagszerkezetének hatása az anyag mechanikai tulajdonságaira, 2014
5. Hidi Szilárd: Polimer keverékek szétválasztása és morfológiai vizsgálata újrahasznosítás céljából, 2013
6. Szabó Diána Katalin: Kompatibilizálószer hatása polimer keverékek szétválasztása esetén, 2013
7. Molnár Ádám: Kompatibilizálószer hatása polimer keverékek mechanikai tulajdonságaira, 2013
8. Halmi Bálint: Kompatibilizálószer hatása polimer keverékek morfológiai tulajdonságaira, 2013

Széchenyi István University, Győr:

9. Bella Tamás: Újrahasznosított PET kristályosságának hatása a tulajdonságokra, 2015
10. Vénusz Adrián: Csomagolóanyag újrahasznosítása autóipari termékként, 2014
11. Józsa Imre: PET újrahasznosítása polimer blendekben, 2013

MSc final project

Budapest University of Technology and Economics:

1. Kozák Marianna: Újrahasznosított polietilén-tereftalát fizikai habosítása2016 folyamatban
2. Suba Tamás: Polietilén-tereftalát kristályosságának vizsgálata, 2016 folyamatban
3. Gere Dániel: Adalékanyagok és keverékek hatása a polimerek reológiai tulajdonságaira a fizikai újrahasznosítás során, 2016 folyamatban
4. Budinszki Balázs: Polimerek ömledékállapotú, centrifugális erőtérben történő szétválasztásának vizsgálata és az alkalmazott berendezés fejlesztése, 2016
5. Lovas Zoltán: PET fóliák vizsgálata és fejlesztése, 2016
6. Kóczán Gábor: Reciklált PET-ből értéknövelt műszaki műanyag előállítása, 2014
7. Szilágyi László: A feldolgozási paraméterek és az összetétel hatása polimer keverékek morfológiai és mechanikai tulajdonságaira, 2014
8. Szabó László: Adalékanyagok hatása polimerkeverékek szerkezetére és tulajdonságaira, 2013
9. Turfa Eszter: Extrudált szigetelőlemez előállítása műanyaghulladékból, 2013
10. Molnár Béla: Polietilén-tereftalát habosításának vizsgálata, 2013
11. Rangics Veronika: Égésgátolt reciklált PET habok fejlesztése, 2013

PhD dissertation

1. Molnár Béla: PET palackok csomagolástechnikai célú újrahasznosítása (Supervisor: Ronkay Ferenc), 2014-folyamatban
2. Dobrovszky Károly: A feldolgozási paraméterek hatása a polimer blendek tulajdonságaira (Supervisor: Ronkay Ferenc), 2012-2016, munkahelyi vitán elfogadva, bírálatra benyújtva

University textbook

Ronkay Ferenc, Dobrovszky Károly, Toldy Andrea: Műanyagok újrahasznosítása. Budapesti Műszaki és Gazdaságtudományi Egyetem Gépészmérnöki Kar, Budapest, 2015. 135 p. részben színes ; ISBN 978-963-313-134-3

3.3. Utilization of results

Results of research project are utilized by Jász-Plasztik Kft:

- Development of quality control on waste PET washing and sorting line /Jászapáti operating site, capacity: 2500 kg/h/ by separation in a melted state
- Optimization of recycled PET sheet production and thermoforming /Nagyréde operating site, capacity: 3000 kg/h/ using chemical foaming agent
- Injection molded TV parts were produced using flame-retardant recycled PET as raw material.

Reference contact: Mr. Lajos Kasza executive director

Budapest, 30 September 2016 Dr. Ronkay Ferenc