Morphological and Mechanical Properties of Injection Molded Recycled Poly(ethylene terephthalate) Samples

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Abstract. Recycled poly(ethylene terephthalate) (PET) was made by extrusion from original PET, and after that injection samples were made. Morphological properties of the samples and regranulates, and mechanical properties of the samples were investigated until fourth week after the produce. The crystalline fraction of regranulates did not change, while the crystallinity of the injection molded samples increased during four weeks. Mechanical properties (tensile stress, modulus, and impact strength) had significant changes during four weeks. Connections between morphological structure and mechanical properties were found.

INTRODUCTION

Recently recycled PET is used as secondary raw material for textile-, packaging- and engineering applications. This is permitted of increasing amount of the waste, and the better processing technologies (e.g. more effective waste cleaning technologies, processing methods) [1]. There are lot of researches of different applications of recycled PET (beside the fiber and food packaging industry), for example blends [2], composites [3], mortars [4] and concrete [5] in building industry. An important application can be the injection molded mechanical parts, because of the amount of PET waste, and good mechanical properties of PET. There are researches in this field, too [6], but there are a lot of uninterpreted phenomenon.

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 [7].

The aim of this study was to investigate the morphological and mechanical properties of injection molded recycled PET samples. 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. Connections between the morphological structure and mechanical properties were found.

EXPERIMENTAL

In this study PET NeoPET80 with 0.8 dl/g intrinsic viscosity (IV), supplied by NeoGroup (Lithuania) was used. Recycled PET (RPET) was made by extrusion, modeling properties of the commercial recycled PET without any contamination. Two kind of regranulates were made RPET1 (once extruded, IV=0.68 dl/g) and RPET2 (twice extruded, IV=0.51 dl/g).

Before the injection molding RPET1 was dried at 160°C for 4 hours in Hereaus UT20 hot air drying oven. The injection molded samples were made by Arburg Allrounder Advance 370S injection molding machine. The samples

have 80x80 mm surface and 2 mm thickness. From these samples for the mechanical tests specimens with 10 mm width were cut.

The intrinsic viscosity of the raw material, regranulates and the samples were measured by PSL Rheotek RPV-1 solution viscosimeter at 30°C, using 60/40 wt% phenol/1,1,2,2,-tertrachloroethane as solvent.

Morphological properties were determined by DSC measurements, using Setaram DSC Evo131, with 10°C/min heating rate, in 30-290°C temperature range. In case of granulates some pieces of granulates (4-8 mg) were analyzed, in case of the injection molded samples the core and the skin layer of the product were investigated. The crystallinity of the samples were calculated by equation:

$$KRF = \frac{\Delta h_m - \sum \Delta h_{cc}}{\Delta h_m^0} 100\%$$
(1)

where *KRF [%]* is the relative crystallinity of the sample, Δh_m *[J/g]* is the measured mass specific heat flow during the melting (area of the melting peak), Δh_m *[J/g]* is the measured mass specific heat flow during the cold-crystallization (area of the cold-crystallization peak), Δh_m *[J/g]* is mass specific heat flow of the 100% crystalline PET (140.1 J/g) [7]. The mobile amorphous fraction were determined from the heat capacity step at the glass transition, calculating by equation:

$$MAF = \frac{\Delta c_p}{\Delta c_p^0} 100\%$$
(2)

where *MAF [%]* is the relative mobile amorphous fraction of the sample, Δc_p *[J/g°C]* is the measured mass specific heat capacity jump at the glass transition, Δc_p^0 *[J/g°C]* is the mass specific heat capacity of the 100% amorphous PET (0.405 J/g°C) [7] at the glass transition. The rigid amorphous fraction were calculated by equation:

$$RAF = 100 - MAF - KRF$$
(3)

where *RAF [%]* is the relative rigid amorphous fraction of the sample, *MAF [%]* is the relative mobile amorphous fraction of the sample, *KRF [%]* is the relative crystallinity of the sample.

Tensile tests were carried out on an Instron 3369 universal testing machine. Tensile modulus was calculated between 0.05 and 0.25% strain, with 1 mm/min crosshead speed. Tensile stress was determined using 10 mm/min crosshead speed. In every measurement at least 5 specimens were tested.

Impact strength were determined by Izod impact test, with 2,75J pendulum. In every measurements at least 10 specimens were tested.

Measurements were being carried out during 4 weeks after the producing of the regranulates and the samples.

RESULTS AND DISCUSSION

Morphological Properties of the Regranulates

Figure 1. shows the crystalline fraction of the two kind of regranulates with different average molecular weight. The IV has an effect on the crystallinity, but it does not have on changes of the crystallinity until the fourth week. The lower average molecular weight caused higher crystalline fraction, because of the more mobility and less secondary bonds between the polymer chains. The crystallinity does not show significant change during four weeks after the extrusion.

Morphological and Mechanical Properties of the Injection Molded Samples

Figure 2. shows changes of the crystalline (CRF), mobile amorphous (MAF) and rigid amorphous fractions (RAF) and these changes in the skin layer of the injection molded samples in function of time after manufacturing. The crystallinity of the samples increased from 4% to 12% during the 4 weeks of the measurement, but the crystallinity of the regranulates had decreased. In line with this the rigid amorphous fraction had 20% decrease, and the mobile amorphous fraction had 15% increase. This points to the fact that the chain segments in the rigid amorphous fraction

increase the size of crystals. During the realignment the rigid amorphous phase secondary bonds break and evolve, so the amount the mobile amorphous fraction can increase.

Figure 3. shows the morphology results of the skin layer of the samples. Similarly to the core layer the three phases show same trends, the crystalline fraction increased, from 4% to 10%. The MAF and RAF did not show the trend like in case of the core layer. The RAF decreased, but not significantly. The MAF decreased in contrast with the core layer.

According to morphological test the main cause of the post-crystallization of the injection molded samples was not the morphological structure (IV, molecular weight) of the raw material (regranulate), because the crystallinity of the regranulates did not change after the extrusion. The possible reason of significant increase of the crystalline fraction of the samples is the morphological structure evolved during injection molding (skin-core layers, oriented parts, etc.). This structure depends on the technological parameters, like mold and melt temperatures, cooling rate, injection speed (shear rate), packing pressure, etc.

Figure 4. shows the tensile properties of the injection molded samples. The tensile stress increased from 50 MPa to 58 MPa, the tensile modulus increased from 2140 MPa to 2230 MPa until the fourth week after producing. Increase of the tensile strength can be caused by increase of the crystallinity. Higher crystalline fraction can result higher strength, because of the better mechanical properties of the crystalline structure (compared to the amorphous one). On the other hand, as a result of post-crystallization, the amorphous phase can change its structure. The chain segments in the RAF enlarge the size of a crystal, and it can cause a stretching effect on the segments in the MAF. As a result of this stretching MAF can be more oriented then before post-crystallization. This orientation can increase the tensile strength, too.

Figure 5. shows the impact strength of the samples, which decreased from 4.3 kJ/m^2 to 3.5 kJ/m^2 at the fourth week after the injection molding. This change can be caused by increasing the crystalline fraction and crystal size. The crystal grooving during the post-crystallization change the crack propagation, and led to shorter cracking lengths. On the other hand, the flexibility, and the energy absorbing capacity of the samples decreased because of the lower amount of MAF. This effects reduce the impact resistance.

In case of recycling PET the changes of the properties after producing a product are not clearly predictable, but these are very important to know to making products. In this study the morphological and mechanical properties of injection molded samples, and these changes after the produce were investigated.

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 from 50 MPa to 58 MPa. This can be caused by orientation of the MAF and increase of the CRF. The tensile modulus increased from 2140 MPa to 2230 MPa, which is caused by orientation of the MAF during the post-crystallization. The impact strength decreased significantly, from 4.3 kJ/m^2 to 3.5 kJ/m^2, due to decrease of the elasticity of the samples, and increase of the crystal sizes.

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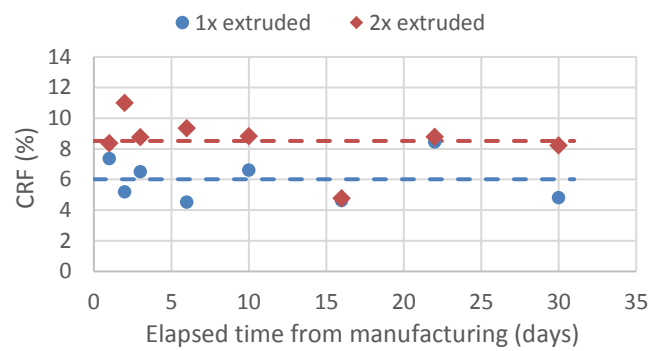7. J. D. Badia, E. Strömberg, S. Karlsson and A. Ribes-Greus, Polym. Degrad. Stabil. **97**, 98–107 (2012).

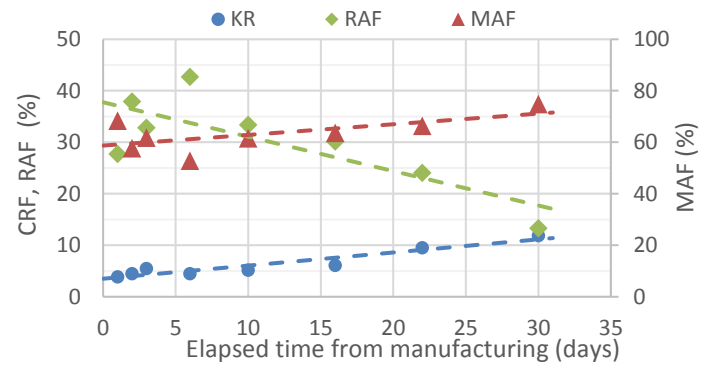**Figure 1.** Crystallinity and its changes of the regranulates

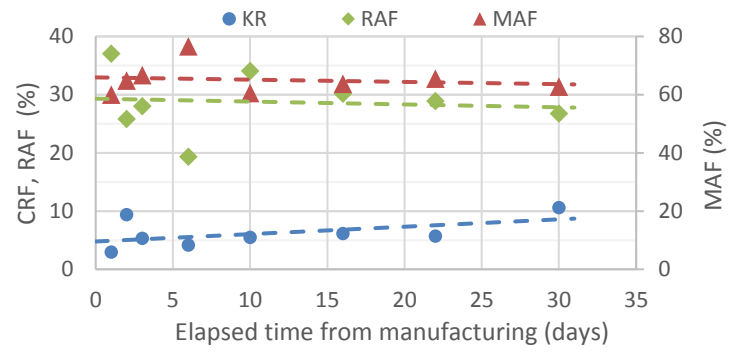**Figure 2**. Morphological properties of the core layer of the samples

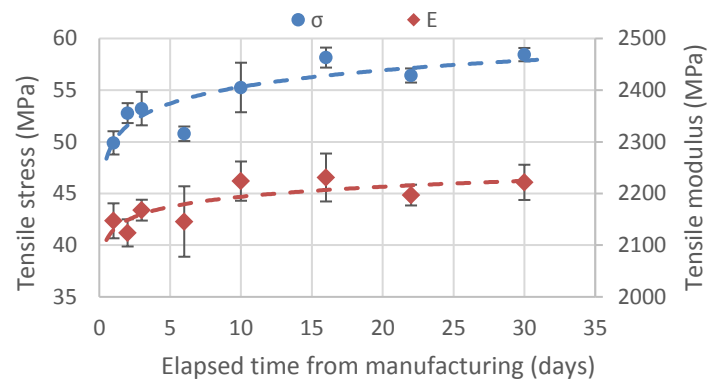**Figure 3.** Morphological properties of the skin layer of the samples
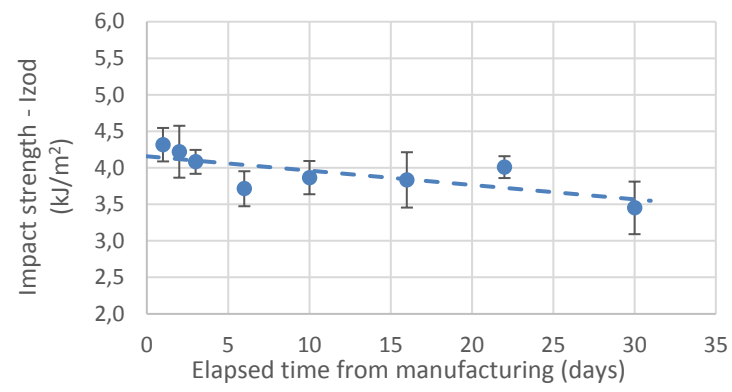
Figure 4. Tensile properties of the samples

Figure 5. Impact strength of the samples