

Improvement of mechanical properties of recycled PET by reactive toughening and post-crystallization

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Abstract: Noticeable increase in impact strength of recycled PET (RPET) was achieved using ethylene-butyl acrylate-glycidyl methacrylate (EBA-GMA) type reactive terpolymer (PTW). The decrease in stiffness and heat resistance due to reactive toughening was successfully compensated by thermal annealing. Based on the results, strong correlation can be shown between crystallinity and impact strength: increasing crystallinity results in reduced impact resistance at PTW contents higher than 5 m/m%, yet a 6-time increase compared to 100 % crystallized RPET was reached with 15 m/m% PTW content. Regarding heat resistance and stiffness, crystallinity appears to be the key parameter: above a critical value of 10 % crystallinity a sharp improvement of the properties can be noticed. Based on the results, properly choosing the elastomer ratio and post-crystallization conditions, post-consumer PET can be suitable for durable engineering applications as well.

Keywords: recycling; poly (ethylene terephthalate); reactive toughening; crystallization

I. INTRODUCTION

Poly (ethylene terephthalate) (PET) is one of the commodity plastics that are applied in the largest quantity: in 2020, 70 million tonnes was produced [1]. One of its main applications is the packaging industry where plastic bottles are produced, which after a short life cycle become waste. Annually 1.4 – 1.6 billion PET bottle waste is generated, from which only 35% is recycled [2]. Its application as a durable engineering plastic, however, is limited, due to its brittleness and the low heat resistance in amorphous phase.

Semi-crystalline PET has a low impact resistance therefore it fades to the background in the engineering plastic fields. Toughening is a possible solution for this problem, which can be carried out by compounding the polymer with elastomers, or by copolymerization [3]. Billon and Meyer [4] studied the toughening of amorphous and semi-crystalline PET with core-shell particles. For their experiments, high-intrinsic-viscosity (IV) PET and two core-shell particles were used. The latter have similar chemical structures: butyl acrylate core and PMMA shell. One of the toughening agents had reactive epoxy groups on their shell to promote the linkage of elastomer and

PET ends of chain, while the other agent did not contain reactive groups. Based on their research, it can be concluded that the toughening effect of core-shell nodules is based on the formation of cavitation voids, which cause local disturbance in the stress field of the sample, so plastic deformation or other energy dissipating fracture mechanism occurs. It is important to note, that while both elastomer systems could successfully toughen amorphous PET, the effective toughening of semi-crystalline polymer was only possible with sufficient adhesion and homogenous dispersion of the elastomer particles, which can only be achieved by reactive toughening.

In another study Bocz et al. [5] examined the effect of the molecular weight (MW) of PET matrix on the toughening efficiency. By applying recycled PET (RPET), the increased number of reactive terminal groups and shorter, but more mobile chains enable to reach prominent impact strength with lower elastomer content (10 m/m%), while original PET requires higher ethylene-butyl acrylate-glycidyl methacrylate (EBA-GMA) content. Short-chained, reactive RPET molecules provide better dispersion of the elastomer, as more chemical bounds can be formed between the polymer and the toughening agent. Even though impact strength greatly

improves, other mechanical properties (stiffness) decreases. Continuing the previous study, Ronkay et al. [6] analysed the impact of the water content of PET on toughening, and noticed that a certain amount of water during melt processing promotes hydrolytic degradation which creates the reactive, short-chained PET fraction that is necessary for effective reaction with EBA-GMA. As a result, almost 6 times higher notched impact strength was achieved simply by omitting the conventional drying step before processing the polyester.

PET can be crystallized due to its chemical and geometrical regularity. The crystallinity and the morphology of the structure strongly effects the polymer's properties. Higher crystallinity results in higher glass transition temperature (T_g): the T_g of amorphous PET is 65-70 °C, while the semi-crystalline PET's T_g is 15-20 °C higher than that. Besides, semi-crystalline polymers have higher modulus, tensile strength, hardness and have higher resistance against solutions, but their impact properties are poor [7].

Loyens and Groeninckx [8] examined the effect of matrix properties (MW, crystallinity) and temperature on the impact resistance of elastomer toughened semi-crystalline PET. The dispersed phase was ethylene-propylene copolymer (EPR), besides, ethylene and 8 m/m% glycidyl-methacrylate (E-GMA8), latter served as a compatibilizing agent. When no compatibilizer was applied, the structure was rough, regardless the MW. E-GMA8 significantly reduced the size of the dispersed phase, but further increasing its ratio did not lead to notable change at low and medium MWs. In contrast, high MW materials showed stronger dependence on dispersed phase concentration and composition. Latter can be explained by the reduced number of end-groups, which results in fewer interfacial grafts.

It can be concluded, that the MW of the matrix significantly affects both crystallization and PET-GMA interaction [5,8]. RPET is more favourable from both aspects than original PET, because of the short-chained fraction. The proper dispersion of the elastomer particles and the developing morphology are key to sufficient toughening: the finer the structure, the better the impact resistance. Crystallinity affects both mechanical and thermal properties, moreover the ratio of rigid amorphous phase also influences the properties according to the three-phase model [9].

Previous studies proved that RPET can be toughened by EBA-GMA type terpolymer (PTW) PTW more effectively and better impact strength results can be achieved compared to original PET [5], however stiffness and rigidity decreases. The aim of the study is to simultaneously improve impact resistance and stiffness with PTW and post-crystallization. By optimizing the mechanical

properties of RPET, new, potential application areas will open, thus it can be a promising alternative to structural polymers such as acrylonitrile butadiene styrene (ABS) or polycarbonate (PC).

II. MATERIALS AND METHODS

As for the recycled material, industrial quality recycled PET flakes (RPET) were applied (JP Pack Kft., Hungary), which had 0.56 ± 0.03 dl/g IV value and $M_w = 16\,900$ g/mol, as measured by GPC [5]. The recycled polymer was from packaging used in food industry: the grinded excess material from sheet extrusion and thermoforming. As toughening agent, Elvaloy PTW (DuPont, USA) (PTW) which consists of 66.75 m/m% ethylene, 28.00 m/m% butyl acrylate and 5.25 m/m% glycidyl methacrylate, was applied as reactive toughener. The melt flow index of PTW is 12 g/10 min (190 °C / 2.16 kg), its melting point is 72 °C and has a glass transition temperature at -55 °C [10]. Based on our previous research [5], PTW was applied in RPET matrix at 0, 5, 10 and 15 m/m%, respectively.

Compounding was carried out by LTE 26 - 48 (Labtech Scientific, Thailand) type, twin-screw extruder. The polymer was dried for 3 hours at 160°C prior to processing, then the temperature was lowered to 90 °C and the PET was dried for additional 1 hour. Decreasing the drying temperature was necessary to prevent the premature melting of PTW. Zone temperatures varied from 250°C to 260°C, and the screw speed was 90 rpm with 40% relative engine performance. The processing parameters (zone and die temperatures, screw speed) during compounding were kept constant at each composition. It can be observed in Table 1, that under these conditions the die pressure increased linearly with increasing PTW content, which indicates chemical reaction taking place between the blend components. However, changing the processing conditions was not necessitated.

Table 1. Die pressures during compounding

<i>PTW content (%)</i>	<i>Die pressures (bar)</i>
0	43
5	47
10	49
15	56

After 4 hours of drying the granules were injection moulded 60 mm x 60 mm x 2 mm plaques by Mitsubishi 50MetII injection moulding machine. The zone temperatures changed from 245 °C to 255 °C and the mould temperature was 40 °C. holding pressure was 50 MPa and lasted for 4 s.

The injection moulded plaque specimens were annealed at a preheated Memmert Une 200 drier, at 150°C, between two aluminium mould plates for 180 s.

10 mm wide specimens were cut from the injection moulded plaques, notched, and tested by Izod impact tester at room temperature. Pendulum energy was 5.5 J, and the no-load loss was 0.02 J.

The quasi amorphous and semi-crystalline samples were examined by DSC in nitrogen atmosphere. The temperature ranged from 20°C to 320°C and the cooling rate was 20°C/min. The original crystallinity of the material was determined from the heating curve in accordance with the following equation (1):

$$CRF = \frac{\Delta h_m - \Delta h_{cc}}{\Delta h_m^0 \cdot (1 - w_{PTW})} \cdot 100\% \quad (1)$$

Where CRF (%) is the calculated crystallinity, Δh_m (J/g) is the area of the mass specific melting peak, Δh_{cc} (J/g) is the area of the mass specific cold crystallization peak, Δh_{m0} (J/g) is the mass specific enthalpy of 100% crystalline PET and w_{PTW} (-) is the weight ratio of PTW.

Dynamic mechanical analysis (DMA) in tensile mode was performed on the 30 mm x 8 mm x 2 mm specimens with 10 Hz frequency. The temperature ranged from 10°C to 140 °C, and the heating rate was 3 °C/min. The distance between the grips was 20 mm.

III. RESULTS AND DISCUSSION

1. Effects of the elastomer content and thermal annealing on the mechanical properties

PTW is a well-known toughening agent, which has already been applied to PET blends successfully [5,6]. The notched Izod impact strength of the RPET samples with increasing PTW contents before and after crystallization are presented in **Fig. 1**.

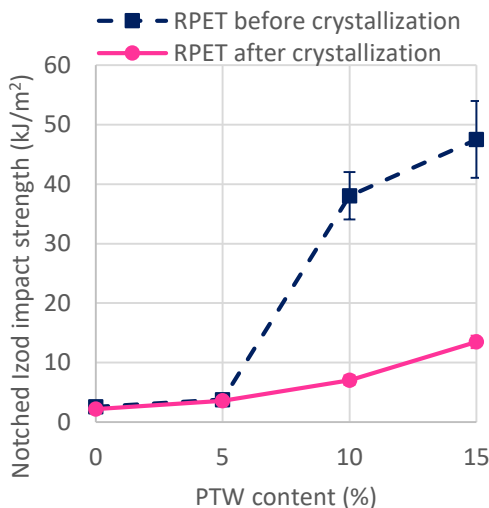


Figure 1. Notched Izod impact strength as the function of PTW content

The elastomer is efficient for the amorphous samples above 10 m/m% of PTW, where a sharp increase in the impact strength can be seen. The results further improve with the addition of 15 m/m% PTW. This can be explained by the short chains in RPET which form an effective toughening enhancer interphase [5] in the presence of the reactive elastomer. The crystallized specimens show a different tendency: the impact strength gradually increases with increasing elastomer ratio. Crystallization clearly effects the impact resistance above 5 m/m% PTW content, as the values decrease by 75 % after crystallization, but with 15 m/m% PTW content the impact strength is still 6-times higher than that of 100 % crystallized RPET. At lower elastomer ratios impact strength barely changes.

Fig. 2 illustrates the storage modulus at room temperature (23°C) as the function of PTW content. A decreasing linear correlation between the two parameters can be observed. After crystallization the parameters still show linear correlation. Compared to the amorphous samples, a 20 % increase in storage moduli can be seen, which means that the post-crystallization improved the stiffness.

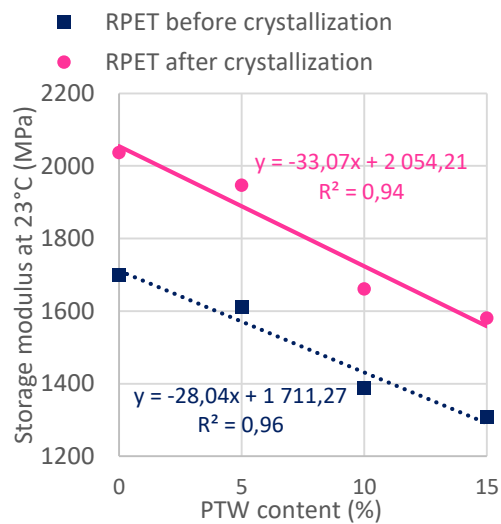


Figure 2. Storage modulus (23°C) as the function of PTW content

Storage modulus at 90°C is in connection with the heat resistance of the material. These values are presented as the function of PTW content in **Fig. 3**. Before crystallization the storage moduli are relatively low (between 4-8 MPa), but a great enhancement can be achieved by the 3-minute crystallization. As a result, the storage moduli values reach 400 – 600 MPa, which is a two orders of magnitude increase. The elastomer content significantly decreases the stiffness, as **Fig. 2** and **Fig. 3** show it.

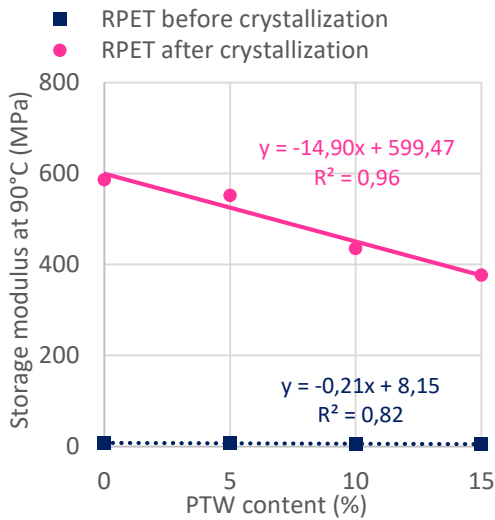


Figure 3. Storage modulus (90°C) as the function of PTW content

2. Effect of the elastomer content and the post-crystallization on the morphology

Crystallinity was determined by DSC analysis, and the results are presented in Fig. 4. Before the crystallization the value of initial crystallinity is between 8 - 10 %, which is not significantly influenced by the PTW content. However, after the crystallization the values moderately increase with the PTW content from 24 to 26%. This indicates that PTW does not really affect the crystallization process. The crystallization time appears to be efficient: the crystallized 100 % RPET has appr. 17 % increase in relative crystalline fraction.

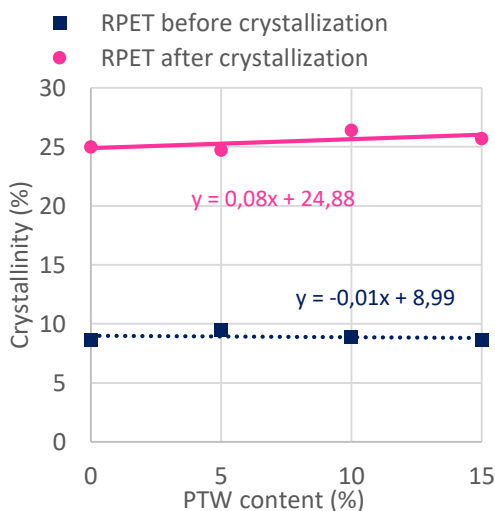


Figure 4. Crystallinity as the function of PTW content

Fig 5 presents the glass transition temperatures (T_g) as the function of PTW content. A slight decrease in the values can be observed as more elastomer is added to the samples. However, thermal annealing has a more significant effect, as T_g increases by 15°C after crystallization.

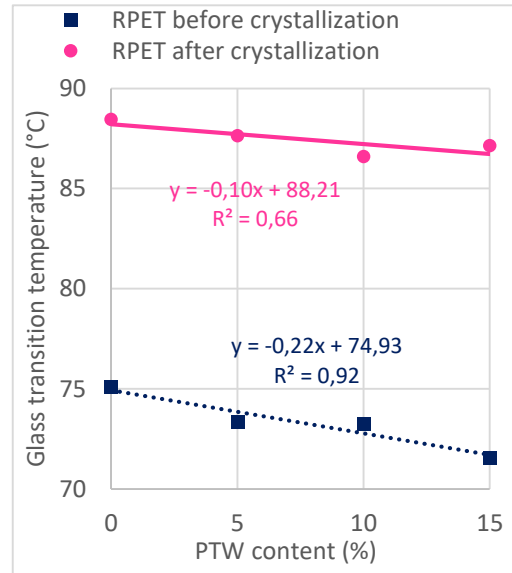


Figure 5. Glass transition temperature as the function of PTW content

Fig. 6 shows the connection between storage modulus (at 23°C) and crystallinity. Samples with the same PTW content have a great difference in their storage modulus. The performance of the ones with higher crystallinity is much better: the improvement is appr. 300 MPa.

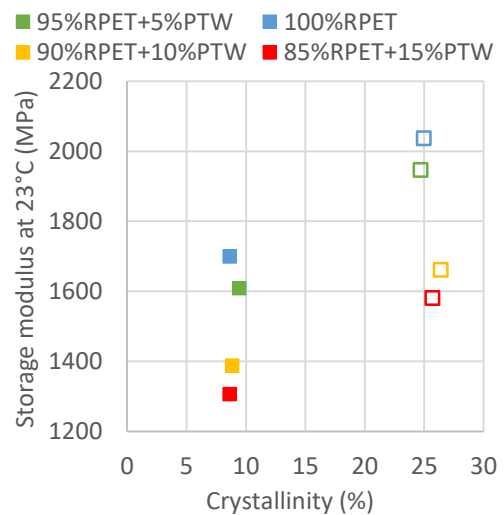


Figure 6. Storage modulus (23°C) as the function of crystallinity: before crystallization: ■, after crystallization: □

Fig 7 shows a similar trend: the storage moduli at 90°C are lower when the crystallinity is below 10 %, and a sudden, significant increase can be noticed at higher crystallinity rates. Figs. 6 and 7 suggest that a critical crystallinity level is required to achieve enhanced stiffness and heat resistance.

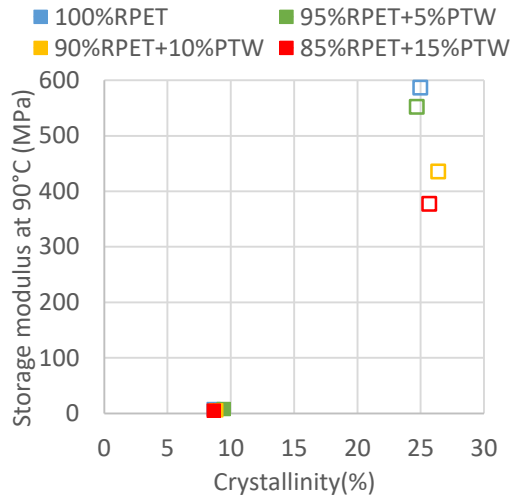


Figure 7. Storage modulus (90°C) as the function of crystallinity: before crystallization: ■, after crystallization: □

Notched Izod impact strength significantly decreases with crystallinity if the PTW content is 10 m/m% or higher, as it is indicated in Fig. 8. At lower elastomer ratios the initial impact resistance does not change significantly with crystallinity.

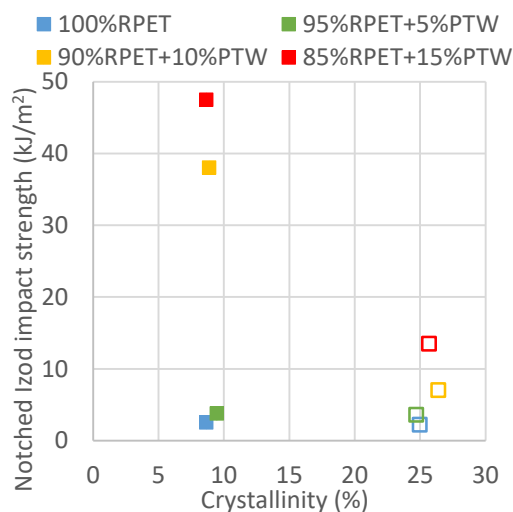


Figure 8 Notched Izod impact strength as the function of crystallinity: before crystallization: ■, after crystallization: □

Fig. 9 shows that the impact strength is inversely proportional to the storage modulus at 23°C. Crystallized samples have relatively high storage

moduli, while the uncrystallized ones with higher PTW content, have outstanding impact resistance.

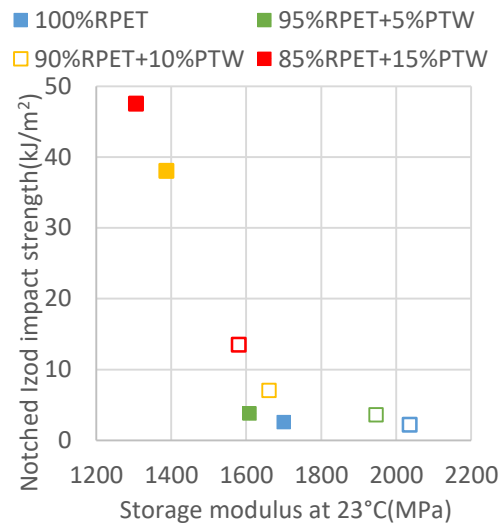


Figure 9. Notched Izod impact strength as the function of storage modulus (23°C: before crystallization: ■, after crystallization: □)

IV. CONCLUSIONS

For successful toughening of RPET, at least 10 m/m% PTW is required, which results in a 15-fold increase in impact strength compared to 100 % RPET. 15 m/m % PTW provides an even better toughening, with almost 19 times better results. After thermal annealing, storage moduli at 23°C increased by 250-300 MPa, and by 70 times at 90°C. By post-crystallizing the samples at 150°C for 3 minutes each composition reached 24 – 26 % crystallinity. Annealing deteriorates the effect of PTW, and impact resistance values decrease compared to the non-crystallized samples. However, higher PTW contents still resulted in better toughening properties. Even though post-crystallization decreased impact resistance, it greatly enhanced stiffness and heat resistance.

Based on the results, altering the additive ratio and the post-crystallization, it is possible to develop heat-resistant and stiff injection moulded PET products from bottle scrap, with balanced toughness, thus suitable for engineering applications.

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AUTHOR CONTRIBUTIONS

E. Slezák: Experiments

F. Ronkay: Conceptualization, analysis of the results

K. Bocz: Supervision, Review and editing.

DISCLOSURE STATEMENT

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

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