The Effect of the Compatibilizer SEBS-g-GMA on the Blend PP-PET: Virgin and Recycled Materials

Karen Van Kets [a], Nicolas Van Damme [a], Laurens Delva [a] and Kim Ragaert [a]

[a]Center for Polymer & Material Technologies, Department of Materials Science & Engineering, Faculty of Engineering & Architecture, Ghent University. Technologiepark 915, B-9052 Zwijnaarde

Presenting author: ncvdamme.vandamme@ugent.be
Corresponding author: kim.ragaert@ugent.be

Abstract. In the carpet industry poly(ethylene terephthalate) (PET) and poly(propylene) (PP) are often used together within a single product. Mechanical recycling of these carpets results in a blend of PET and PP, which are immiscible. To enhance impact strength of this waste stream, the compatibilizer SEBS-g-GMA was used. More specific the transferability of earlier results with the compatibilizer, obtained on virgin PET-PP blends with amorphous PET (PETg), was assessed. Firstly, from these blends to blends with semi-crystalline PET (PETe) and secondly, from virgin to recycled materials. Two blends of virgin material were made containing 80 wt% PP and 20 wt% PETg or PETe. The effect of adding 2,5 wt% SEBS-g-GMA was assessed. Subsequently, post-industrial PP (r-PP) and post-consumer PETe (r-PETe) were blended and mechanical properties were measured for blends with and without compatibilizer. An increase in impact strength for the two virgin compatibilized blends (PP:PETg:SEBS-g-GMA and PP:PETe:SEBS-g-GMA) was expected and confirmed. A reduced effect of the compatibilizer on impact strength was observed for the recycled blends, due to the possible presence of contaminants. It was concluded that the results from virgin PETg-PP were directly transferable to virgin PETe-PP, but not entirely to recycled materials.

Keywords: recycling, compatibilizer, mechanical properties, morphology, polypropylene, poly(ethylene terephthalate)
PACS: 81.05.Lg, 81.20.Hy, 81.70.Bt, 83,80Tc

INTRODUCTION

When poly(ethylene terephthalate) (PET) and poly(propylene) (PP) are used for carpet manufacturing, the polymers are attached to one another and become physically inseparable for the purposes of mechanical recycling. Typically, such blends of polar and apolar polymers are inherently immiscible, which leads to reduced mechanical properties of the resulting product, toughness foremost among them [1]. In this It was the aim of this research to recover the blend's properties by increasing the miscibility via the use of a compatibilizer. there has been attempted to increase the toughness. A blend with a matrix of 80 wt% PP and a dispersed phase of 20 wt% PET was made. The main goal was to obtain a tougher material (and consequently also a higher elongation at break) and second to evaluate the influence of the compatibilizer on the yield strength.

The morphology and composition can give a prediction for the mechanical properties. If the amount of the dispersed phase is too high, the PET spheres enlarge and will present a bigger surface. The stress transfer at the interface between both polymers will decrease due to the weak interfacial adhesion and a wider interface. This results in reduced mechanical properties for the blend. On the other hand, if the amount of the dispersed phase is too small, the inter-particle distance becomes too high, which causes a more fracture sensitive material [2, 3].

Because these two polymers are immiscible in the melt state, the compatibilizer styrene-ethylene/butylene-styrene grafted with glycidyl methacrylate (SEBS-g-GMA) was added. This compatibilizer was selected by previous research [4], where it was found to sufficiently induce the brittle-to-ductile transition for an added percentage of 2,5 wt% to a mix of 80:20 PP with amorphous PET (PETg). SEBS-g-GMA increases the toughness and is made from a rubber component grafted with a functional group. It will act as an impact modifier and as coupling agent [5]. The different interactions between the compatibilizer and PET are an in-situ copolymerisation of epoxy ring-opening with the end-groups of PET. But also hydrogen bridges between the carboxylgroups, dipole-dipole interactions and Van Der Waals interactions can occur. PP is the matrix and only the Van Der Waals interactions are possible with the ethylene/butylene components of the rubber [1, 6, 7].

In this research the transferability of the compatibilizer's effect from PP:PETg blends to blends consisting of PP and semi-crystalline PET (PETe) was examined, as well as the transferability from these virgin to recycled industrial materials. The difference of completely amorphous PETg and semi-crystalline PETe is originated in a different backbone structure of the polymers. PETe is the common known condensation polymer from ethylene glycol and terephtalic acid. While the ethylene glycol in PETg is replaced by a diol with increasing free volume. This can be propylene glycol, but more often 1,4-bis(hydroxymethyl) cyclohexane is used [8, 9].

MATERIALS AND METHODS

Materials

All blends of PP and PET were mixed manually before adding them to the co-rotating twin-screw extruder (Coperion ZSK 18, 40 L/D) Compounding was performed at a temperature of 280°C, as preliminary research showed that melt compounding at increasing temperatures above the melt temperature improved the impact strength of the compatibilized blend [4]. The blends are named '*matrix* : *dispersed phase* : *compatibilizer*' (78 wt% :19,5 wt% :2,5 wt%). Wherein the matrix is PP or recycled PP (r-PP), the dispersed phase is PET where each time one of the following PET were mixed in the blend: PETg, PETe and recycled PETe (r-PETe). As compatibilizer SEBS-g-GMA was added by the side feeder. The virgin materials used in this project were PP (DOMO: PP Domolen 1040N, density: 0,91 g/cm³), PETg (EASTMAN: Eastar™ Copolyester 6763, density: 1,27 g/cm) and PETe (Equipolymers: PET Lighter C93, density: 1,34 g/cm³). The recycled materials were kindly donated by Beaulieu International Group (BINTG) located in Wielsbeke (Belgium). For all blends test bars were injection moulded (BOY 22S) at the same temperature of compounding and were left at room temperature for minimum five days prior to testing. These test bars include 'dog bone' specimens for tensile (ISO 527-2/1B) and rectangular bars for impact testing (ISO 179-1/1eA).

Methods

In the initial phase of the research, differential scanning calorimetry (DSC)-analysis (NETZSCH DSC 204 from Phoenix) was performed on all the used materials. The density was used to characterise the materials. The density of the melted PET-fibers and the granulates of the SEBS-g-GMA were gravimetrically determined by the immersion method according to ISO 1183. This was executed in propanol by means of a density kit and a Precisa balance. For the recycled materials there was a more profound analysis by Fourier transformation infrared (FTIR) (TENSOR 27 FTIR from Brüker). The different blends were tested on their mechanical properties. First the virgin blends, where the differences of amorphous to semi-crystalline PET were compared and afterwards the recycled blends. The mechanical tests include a tensile and impact test. According to the Charpy method of ISO 179-1/1eA the rectangular test bars were notched 2 mm and tested for impact strength with a pendulum of 2 J. The tensile specimens were tested in accordance with ISO 527 on an Instron 5565 machine with a load cell of 2 kN. An extensometer with gauge length 25 mm was used for strain measurement in the initial part of the test where the Young's modulus is determined. There the cross-head rate of 10 mm/min was used. After removing the extensometer, a cross-head rate of 50 mm/min was applied on the tensile bars. The tensile offset yield at 0.2% (σ_y), strain at break (ε_b) and the Young's modulus (E) were determined (Bluehill2 software).. The reported values for the mechanical properties are the average of at least five measurements. All data was processed with SPSS Statistics 20 and screened for outliers. The outliers were deleted in order to work within the 95% confidence interval. Furthermore the morphology of the blends was examined by scanning electron microscopy (SEM) (Jeol JSM-7600F Field emission) of cryofractured surfaces and briefly the crystallinity was analysed using DSC.

RESULTS AND DISCUSSION

Properties of PP/PETg to PP/PETe (virgin)

It was found that the impact strength and strain at break were similar or increased when comparing the compatibilized blend to the PP matrix. The beneficial effect was even higher when compared to the uncompatibilized blends (Figure 1). The opposite was noted for Young's Modulus and the yield strength. The Young's modulus of the blends without compatibilizer was higher, since the PET had the effect of a filler [10], but their impact strength was weak. A proportional law-of-mixtures could not be used to predict the impact strength results, due to the phase separation effect [11]. It must be noted that the impact strength of PETg was higher than PETe.

The smaller dispersed spheres, the finer dispersion and the smaller inter particle distance, contribute all to a more ductile blend. This can be seen in the SEM-images (Figure 2). Therefore it can be said that the functionality of SEBS-g-GMA is transferable from amorphous PET to semi-crystalline PET.

As the blends with SEBS-g-GMA were compared to the blend without SEBS-g-GMA, the amount of crystallinity in PET decreases due to the copolymerisation between the compatibilizer and the PET during melt blending. This only relates to the semi-crystalline PET. It must be taken into account that SEBS-g-GMA has a high grafting ratio of 1,5 wt%. All the mechanical properties of the blends were compared to the matrix and the results are summarized in Table 1.
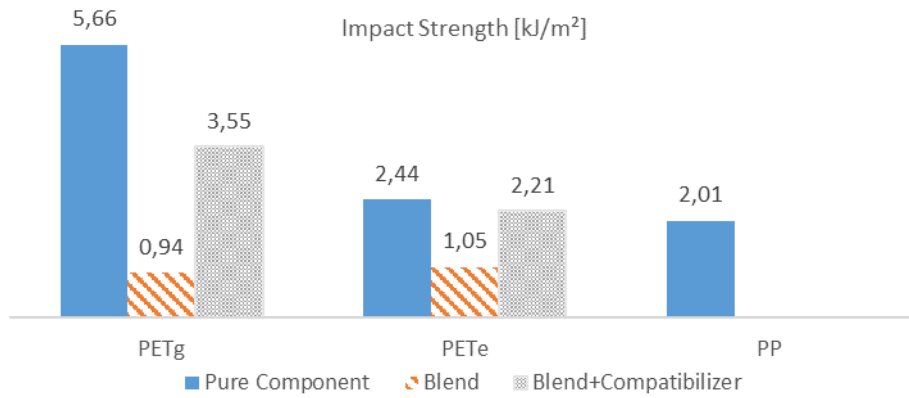
FIGURE 1. The impact strength of the virgin polymers and their blends

Properties from PETe to rPETe

SEBS-g-GMA was also added to a mixture of post-industrial PP (originated form carpet fibres) and post-consumer PET-fibres (origin unknown). The impact strength and strain at break increased with the addition of the compatibilizer, but not as significantly as with the virgin blends. The decrease in yield strength remains within the same trend, as does the Young's modulus but this difference is more pronounced (Table 1). When recycled materials were used, the amount of compatibilizer was insufficient to realize the brittle-to-ductile transition. Possible causes include unknown contamination and additives in the recycled polymers. This was also noticed by Kazemi et al. [12]. The contamination will, according to their interfacial tension, prefer to migrate in one of the polymers or they will prefer to be in the interface. This could cause interaction with the compatibilizer but also influence the migration of the dispersed phase in the matrix phase. Subsequently a different droplet size of the dispersed phase occurred compared to the blend of the virgin materials (Figure 2).

TABLE 1. A summarize of the results from the blends with and without compatibilizer

Material	E [MPa]	σ_y [MPa]	ε_b [%]	Impact strength [kJ/m²]
PP:PETg	1499 ± 116	18,49 ± 0,77	11,51 ± 0,64	0,94 ± 0,00
PP:PETg:SEBS-g-GMA	1134 ± 97	14,29 ± 0,23	34,41 ± 4,92	3,55 ± 0,26
PP:PETe	1628 ± 44	18,33 ± 1,64	16,14 ± 2,05	1,05 ± 0,09
PP:PETe:SEBS-g-GMA	1501 ± 61	14,00 ± 0,48	29,38 ± 0,59	2,21 ± 0,05
PP	1313 ± 100	16,70 ± 1,31	22,92 ± 2,84	2,01 ± 0,15
rPP	1673 ± 26	13,93 ± 0,29	28,48 ± 1,05	2,74 ± 0,18
rPP:rPETe	1926 ± 105	15,69 ± 0,19	12,66 ± 0,84	1,58 ± 0,01
rPP:rPETe:SEBS-g-GMA	1594 ± 38	13,98 ± 0,37	20,83 ± 4,73	1,70 ± 0,05

Morphology of the blends

Besides the smaller dispersed spheres, finer dispersion and smaller inter particle distance; there are other noteworthy remarks to the morphology of the compatibilized blends. These are the increased amount of droplets and a limited particle size distribution (Figure 2), which gives the blend a more uniform consistency than the non-compatibilized blends [13]. This can be correlated to the impact strength results, indicating a matrix with lowered crack propagation and less inducement to micro fractures [2].
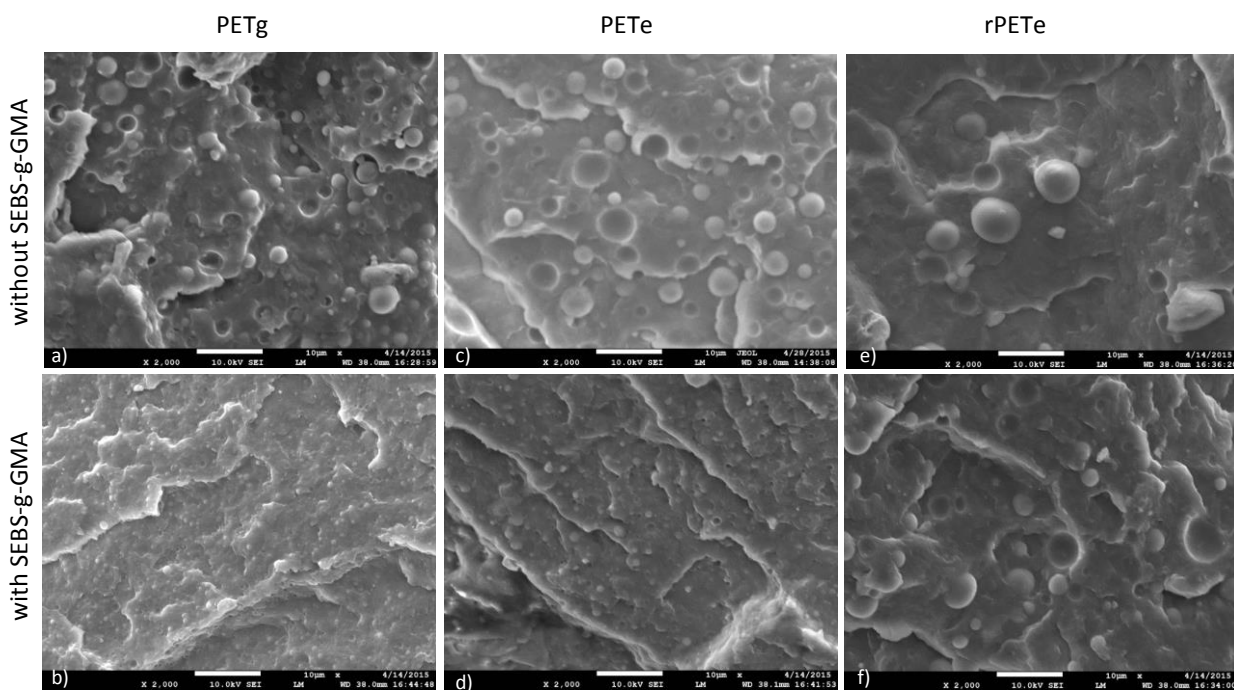
FIGURE 2. SEM-images of all the blends at x2000 magnification with a working distance of 38 mm; the blends without compatibilizer: (a) PP:PETg, (c) PP:PETe and (e) r-PP:r-PETe; the blends with compatibilizer (b) PP:PETg:SEBS-g-GMA, (d) PP:PETe:SEBS-g-GMA and (f) r-PP:r-PETe:SEBS-g-GMA

Conclusion

It can be concluded that the effect of SEBS-g-GMA is transferable from PETg to PETe in PP:PET blends of virgin material. Higher impact strength and larger elongation at break are observed. Due to the coupling effect of the compatibilizer, a better dispersion of PET in the PP matrix and a smaller inter particle distance are effectuated. However the values for impact and elongation at break are bigger for the blend with PETg. Resulting from its amorphous state and the better flow during processing, introducing a better mixture of the two phases.

The effect of the compatibilizer, when using post-industrial PP and post-consumer PET, is much smaller. Recycled material is unpredictable and the presence of contaminants is not exceptional. These impurities are a hindrance for a good dispersion and can interact with the SEBS-g-GMA, causing a decrease in amount of compatibilizer for the main components. Further research will decide the needed amount of compatibilizer for a sufficient brittle-to-ductile transition in r-PP:r-PET blends.

ACKNOWLEDGMENTS

REFERENCES

1. Heino, M., J. Kirjava, and P. Hietaoja, *Compatibilization of polyethylene terephthalate/polypropylene blends with styrene–ethylene/butylene–styrene (SEBS) block copolymers*. Journal of applied polymer science, 1997. 65(2): p. 241 249.
2. Wu, Souheng, *Impact fracture mechanisms in polymer blends: Rubber-toughened nylon*. Journal of Polymer Science: Polymer Physics Edition, 1983. 21(5): p. 699-716.
3. Bucknall, C. and D. Paul, *Notched impact behaviour of polymer blends: Part 2: Dependence of critical particle size on rubber particle volume fraction*. Polymer, 2013. 54(1): p. 320-329.
4. Van Bruggen E., Koster R., Picken S. and Ragaert K., Influence of Processing Parameters and Composition on the Effective Compatibilization of Polypropylene - Poly(ethylene terephthalate) blends. In press in international Polymer Processing..
5. Bicerano, J., A, *Practical guide to polymeric compatibilizers for polymer blends, composites and laminates*. provided by http://www.specialchem4polymers. com, 2005. 22.
6. Koning, C., Van Duin, M., Pagnoulle, C., & Jerome, R., *Strategies for compatibilization of polymer blends.* Polymer Science, 1998. 23(4): p. 707-757.
7. Litmanovich, A.D., N.A. Platé, and Y.V. Kudryavtsev, *Reactions in polymer blends: interchain effects and theoretical problems*. Progress in polymer science, 2002. 27(5): p. 915-970.
8. Schwartz, S., et al., *FIBER PRODUCTION-PET modification with MPDiol glycol*. Chemical Fibers International, 2003. 53(6): p. 445-449.
9. Wu, J.H., et al*., Poly (ethylene terephthalate)/Poly (ethylene glycol-co-1, 3/1, 4-cyclohexanedimethanol terephthalate)/ Clay nanocomposites: Morphology and isothermal crystallization kinetics*. Journal of applied polymer science, 2013. 128(1): p. 487-497.
10. Bataille, P., S. Boisse, and H. Schreiber, *Mechanical properties and permeability of polypropylene and poly (ethylene terephthalate) mixtures*. Polymer Engineering & Science, 1987. 27(9): p. 622-626.
11. Hubo, S., Delva, L., Van Damme, N. &Ragaert, K., *Blending of recycled mixed polyolefins with recycled polypropylene:effect on physical and mechanical properties*. Polymer Processing Society 2015, Graz. Accepted for publication in AIP Conference Proceedings
12. Kazemi, Y., Ramezani Kakroodi, A., & Rodrigue, D. (2015). Compatibilization efficiency in post-consumer recycled polyethylene/polypropylene blends: Effect of contamination. *Polymer Engineering & Science*, 55(10), 2368-2376.
13. Inoya, H., Wei Leong, Y., Klinklai, W., Takai, Y., & Hamada, H., *Compatibilization of recycled poly (ethylene terephthalate) and polypropylene blends: Effect of compatibilization on blend toughness, dispersion of minor phase, and thermal stability*. Journal of Applied Polymer Science, 2012. 124(6): 5260-5269.