Post-consumer Polyethylene Terephthalate and Polyamide 66 Blends and Corresponding Short Glass Fiber Reinforced Composites

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Blends of bottle-grade post-consumer polyethylene terephthalate (PET) and virgin polyamide 66 (PA66), over the complete composition range, and corresponding short glass fiber (SGF) reinforced composites were investigated. These materials were compounded in a twin-screw extruder and injection molded as standard specimens. Morphological investigation of the composites revealed that the short glass fibers have a good size distribution and are homogenously dispersed within a polymeric matrix. The PET/PA66/SGF composites showed good mechanical performance in flexural, tensile and impact tests demonstrating that the addition of SGFs to PET/PA66 blends is an interesting approach to obtaining new thermoplastic composites. In addition, this represents a potential application for post-consumer PET, an abundant and cheap material, in the well-established market of PA66/SGF composites, which are widely used in technical parts requiring high mechanical and thermal properties.

Keywords: PET, PA66, nylon 66, short glass fiber, composite, blend

1. Introduction

Polymer blends reinforced with short glass fibers (SGFs) have received considerable attention from academic and industrial researchers in recent years because these materials can combine the properties of both blends and composites. Success in attaining the target properties of these materials is dependent on several morphological aspects including the polymer blend morphology, the glass fiber size and distribution within the polymer blend and the adhesion between the glass fiber and the polymeric matrix.

The blending of bottle-grade post-consumer polyethylene terephthalate (PET) with suitable polymers and/or compounding with SGFs can be used to attain improved properties of the post-consumer PET and broaden the possibilities for its use as an engineering thermoplastic. Cheng et al.2 studied SGF-reinforcement in blends of post-consumer PET and ethylene-butyl acrylate-glycidyl methacrylate (EBA-GMA) copolymer and of post-consumer PET and maleic anhydride grafted polyethylene-octene elastomer (POE-MAH). Karsli et al.3 investigated the effects of SGF-reinforcement on the properties of post-consumer PET and polyamide-66 (PA66). The PET/PA66 blends were agglutinated prior to extrusion, converting them into free-flowing semi-crystallized granules with a bulk density of 0.44 g cm⁻³.

The aim of this study was to prepare blends of bottle-grade post-consumer PET and virgin polyamide 66 (PA66), over the complete composition range, as well as composites of these blends reinforced with 30 wt% of SGFs (PET/PA66/SGF). The microstructure, thermal and mechanical properties of the samples obtained were then investigated. The use of post-consumer PET in PET/PA66/SGF composites is an interesting approach to incorporate this abundant and cheap material into the well-established market of PA66/SGF composites.

2. Experimental

2.1 Materials

The PET was supplied as bottle-grade flakes by the company Repet (Brazil) and had an intrinsic viscosity of 0.74 dL g⁻¹ (ASTM D 4603[15]). The PET flakes were agglutinated prior to extrusion, converting them into free-flowing semi-crystallized granules with a bulk density of 0.44 g cm⁻³. The PA66 was commercial grade (Radilon® A 27D) and supplied in pellet form by the company Radici Plastics (Brazil).

The short glass fibers (SGFs) used were commercial grade (EC10 4.5 952) E-glass fibers with nominal diameter
of 10 μm containing an epoxysilane surface treatment and were supplied by the company Vetrotex (Brazil) in the form of chopped roving of 4.5 mm length.

2.2 Processing

All materials were dried in a vacuum oven at 80°C for 24 h prior to the processing steps. PET/PA66 blends and PET/PA66/SGF composites were compounded in a TEK TRIL DCT20 intermeshing co-rotating twin-screw extruder, with L/D = 36 and D = 20 mm. The barrel temperature was set at 275°C and the screw speed was 300 rpm. The screw configuration, along with the material feed locations in the extruder, is shown in Figure 1. The screw profile is comprised of two sets of kneading blocks in between conveying sections. The set of kneading blocks upstream was designed to melt and blend the PET and PA66 polymers, whereas the functions of the set of kneading blocks downstream were to disperse and distribute the short glass fibers in the molten polymers. The PET and the PA66 granules were tumbled and fed by a volumetric feeder positioned above the main hopper. Short glass fibers were fed by a volumetric feeder coupled to a side twin screw feeder located before the second set of kneading blocks. The total feed rate was 4.0 kg h⁻¹ and the screw torque level was at around 50% under these conditions.

Table 1 shows the composition of the materials processed in this study. PET/PA66 blends (100/0, 72/25, 50/50, 25/75 and 0/100 by weight) and composites of these PET/PA66 blends with 30 wt% of SGFs were prepared.

Specimens for mechanical tests (ASTM standard bars) were injection-molded from the extruded pellets using an ARBURG ALLROUNDER 270S 400-170 machine under the following processing conditions: barrel temperature profile 230°C-265°C-270°C-275°C-285°C, mold temperature 50°C, flow rate 25 cm³ s⁻¹, holding pressure 500 bar for 7 s and mold cooling time 30 s.

2.3 Characterization

The relative viscosities of the polymers PET and PA66 were estimated in the mixing chamber (Rheomix 600p with roller rotors) of a HAAKE torque rheometer. The analysis was performed at a chamber temperature of 275°C and rotor speed of 100 rpm for 10 min.

Glass fiber lengths in the injection-molded PET/PA66/SGF composites were determined from digital optical images recorded using a Nikon model Coolpix 5400 digital camera, coupled with an Olympus model SZH 10 optical microscope. The images were analyzed using Image J software to estimate the glass fiber lengths in the molded composites. Approximately 400 fibers were examined for each sample. The glass fibers were recovered by burning off the PET/PA66 in an oven at 600°C for 3 hours. The number average length (lₐ), the weight average length (lₘ) and the polydispersity index (P) of the glass fibers were calculated according to Equations 1, 2 and 3, respectively, where nᵢ is the number of glass fibers with length lᵢ and \( \sum \frac{nᵢ}{n} = N \) is the total number of glass fibers.

\[
lₐ = \frac{\sum nᵢ ⋅ lᵢ}{\sum nᵢ}
\]

Figure 1. Screw profile and the feed locations of the twin-screw extruder.

Table 1. Composition of the PET/PA66 blends and PET/PA66/SGF composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>PET content (wt%)</th>
<th>PA66 content (wt%)</th>
<th>SGF content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>100</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PET/PA66 75/25</td>
<td>75</td>
<td>25</td>
<td>—</td>
</tr>
<tr>
<td>PET/PA66 50/50</td>
<td>50</td>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>PET/PA66 25/75</td>
<td>25</td>
<td>75</td>
<td>—</td>
</tr>
<tr>
<td>PA66</td>
<td>—</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>PET/SGF 70/30</td>
<td>70</td>
<td>—</td>
<td>30</td>
</tr>
<tr>
<td>PET/PA66 75/25 with 30% SGF</td>
<td>52.5</td>
<td>17.5</td>
<td>30</td>
</tr>
<tr>
<td>PET/PA66 50/50 with 30% SGF</td>
<td>35</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>PET/PA66 25/75 with 30% SGF</td>
<td>17.5</td>
<td>52.5</td>
<td>30</td>
</tr>
<tr>
<td>PA66/SGF 70/30</td>
<td>—</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>
The critical glass fiber aspect ratio \( (l/d) \_c \) for the effective reinforcement of polymer matrices is given by Equation 4, where \( l \) is the fiber length, \( d \) is the fiber diameter, \( \sigma_f \) is the tensile strength of the fiber and \( \tau_{int} \) is the fiber-matrix interfacial shear strength\(^\text{16} \):

\[
\left( \frac{l}{d} \right) \_c = \frac{\sigma_f}{2 \tau_{int}} \tag{4}
\]

The value of \( \tau_{int} \) can be approximated to the value of the shear stress of the polymer matrix by assuming that there is perfect adhesion between the fiber and the polymer. Taking into account that the shear stress values for the PET and PA66 are around 45 MPa and considering a typical value for the fiber strength of 1500 MPa, it follows that the critical fiber aspect ratio is 17, and thus the critical fiber length is 170 \( \mu \text{m} \) (fiber diameter is 10 \( \mu \text{m} \)), for the effective reinforcement of PET/PA66 blends.

The microstructures of the injection-molded PET/PA66/SGF composites and PET/PA66 blends were examined by scanning electron microscopy (SEM) using a Philips XL30 FEG instrument at an accelerating voltage of 10 kV. The samples were taken from the core of the injection molded bars and cryo-fractured perpendicular to the mold filling. These fractured samples were used to observe the glass fiber distributions in the PET/PA66/SGF composites. To assess the blend morphology, the fractured surfaces of the PET/PA66 75/25 blend and the respective SGF composite were further cryo-polished using a diamond knife and then etched in 85% formic acid to remove the PA66 phase. The surfaces of all samples were sputter coated with gold prior to SEM examination.

The melting events of the PET and PA66 in the PET/PA66 blends and corresponding short glass fiber reinforced composites were determined by differential scanning calorimetry (DSC) using a TA Instruments model Q100 calorimeter. Samples (~9 mg) were taken from the core of the injection-molded bars and heated from 20°C to 300°C at 20°C min\(^{-1} \) under \( N\_2 \) atmosphere (50 mL min\(^{-1} \)). The melting enthalpies for the effective critical fiber aspect ratio is 17, and thus the critical fiber length is 170 \( \mu \text{m} \) (fiber diameter is 10 \( \mu \text{m} \)), for the effective reinforcement of PET/PA66 blends.

The value of \( \tau_{int} \) can be approximated to the value of the shear stress of the polymer matrix by assuming that there is perfect adhesion between the fiber and the polymer. Taking into account that the shear stress values for the PET and PA66 are around 45 MPa and considering a typical value for the fiber strength of 1500 MPa, it follows that the critical fiber aspect ratio is 17, and thus the critical fiber length is 170 \( \mu \text{m} \) (fiber diameter is 10 \( \mu \text{m} \)), for the effective reinforcement of PET/PA66 blends.

3. Results and Discussion

3.1 Microstructure

The glass fiber length distributions in the molded PET/PA66/SGF composites are shown as histograms in Figure 2. The values for the average glass fiber lengths \( l\_f \) (Equation 1) and \( l\_w \) (Equation 2) and the polydispersity index \( P \) (Equation 3) can be seen in the histograms. For all of the composites, similar fiber length distribution patterns were observed, the ranges being 158 \( \mu \text{m} \) to 182 \( \mu \text{m} \) for the \( l\_f \) values, 214 \( \mu \text{m} \) to 230 \( \mu \text{m} \) for the \( l\_w \) values and 1.22 to 1.36 for the \( P \) values. Therefore, the experimental values of \( l\_f \) and \( l\_w \) for the glass fibers in the composites under study (Figure 4) are similar to or higher than the critical value (170 \( \mu \text{m} \) according to the calculations using Equation 4) required for the effective mechanical reinforcement.

Figure 3 shows typical SEM micrographs of cryo-fractured surfaces of the molded PET/PA66/SGF composites, verifying a homogeneous distribution of the glass fibers in the polymer matrices. Another important observation is that the glass fibers are mostly oriented perpendicular to the fractured surface, that is, parallel to the direction of mold filling. Injection-molded short glass fiber filled thermoplastic composites exhibit a complex distribution of fiber orientations along the part thickness, often forming layers, caused by a complex interaction between melt properties and molding conditions. As the melt fills the mold there is a fountain flow which initially orients the fibers and polymer chains perpendicular to the main flow direction. This causes the melt to be deposited on the mold wall with the alignment direction parallel to the mold flow direction. Here it solidifies rapidly and this alignment is retained in the solid part. Further behind the melt front, shear flow dominates and produces fairly uniform levels of fiber alignment. In the very centre of the melt the rate of shear is low and the transverse fiber alignment present at the gate is retained. The final morphology is therefore characterized by the skin layer with small oriented fibers and the core region with low orientation, along with a transition shear zone with high orientation between these two layers, which is simply called skin-core morphology\(^\text{21} \). The micrographs show some holes which are due to the fiber pullout during the cryogenic fracture and can thus be disregarded in the evaluation of the adhesion between the fibers and the polymer matrices.

In general, the composite microstructures verify the efficiency of the mixing in the twin-screw extruder and injection molding, which led to an appropriate degree of dispersion and a homogeneous distribution of the glass fibers in the polymeric matrices.

Another aspect to be considered is the interface between the glass fiber and the polymeric matrix of the composite. The glass fiber used has epoxy pendant groups on the surface which can react with the carboxyl end groups of the PA66.
both PET and PA66 chains during compounding. This leads to coupling reactions between the fiber and the polymeric matrix, regardless of the continuous phase in the polymer blend matrix, which ensure good interfacial adhesion in the composites.

Figure 4 shows typical SEM micrographs of cryo-polished surfaces of a PET/PA66 75/25 blend (Figure 4a) and the corresponding SGF composite (Figure 4b), highlighting the blend morphology. The PA66 domains appear as dark holes in the micrographs because of the etching in formic acid. The phase morphology of the PET/PA66 75/25 blend is comprised of PA66 domains with average size of 0.5 μm dispersed in a continuous PET phase (Figure 4a). This blend morphology is preserved in the corresponding composite (Figure 4b). The good dispersion achieved for the PET/PA66 blend morphology even without a compatibilizer is assigned to the rheological characteristics of the polymers. The low interfacial tension between the PET and PA66 in the melt...
state, which was estimated to be 0.82 mN/m at 275°C using the Wu equation, together with the low PA66/PET viscosity ratio, which was measured to be 1.8 in the mixing chamber of a torque rheometer at 275°C, are favorable conditions for the blend dispersion during the compounding in the molten state. Furthermore, Retolaza et al. have shown that ester-amide interchange reactions are allowed to occur during melt mixing even in the absence of a catalyst, leading to the formation of interfacial compatibilizer agents in the PA66/PET blend.

The morphological aspects mentioned above are essential for ensuring an effective stress transfer from the PET/PA66 matrix to the glass fibers as the composites are mechanically overloaded.

3.2 Thermal properties

The results for the differential scanning calorimetry (DSC) employed to evaluate the overall crystallization of the polymers in the injection molded PET/PA66 blends and PET/PA66/SGF composites are shown in Figure 5.
Figure 5a shows the DSC curves for the blends and composites. The melting of the neat PET and PA66 is represented by endothermic peaks at 249°C and 263°C, respectively. The melting events for the blend-based materials appear as double peaks in the DSC curves since the melting temperatures of the individual polymers are very close. The materials containing PET additionally show a cold crystallization event in the temperature range of 113 to 124°C, indicating that the PET did not fully crystallize during the injection molding process.

To estimate the degree of crystallization of the polymers in the molded materials the melt enthalpies (area below the melting peaks) were subtracted from the enthalpy of the cold crystallization of PET and normalized in relation to the glass fiber content in the case of the composites. For the blend-based materials, the overall crystallization was considered instead of the individual crystallization of the polymers. The melting enthalpies of the molded materials, calculated according to the procedure described above, are shown in Figure 5b. The neat PET showed the lowest value for the degree of crystallization (15%) of the materials investigated and the neat PA66 showed the highest value (35%). This is because the crystallization rate of PA66 is much higher than that of PET; in fact, the low crystallization rate of bottle-grade post-consumer PET is one of the major obstacles in relation to its use as an...
engineering thermoplastic. The melting enthalpies of the PET/PA66 blends shows a synergistic effect in relation to the neat polymers, indicating that the PA66, with a higher crystallization temperature (T_c ≈ 230°C), provides nucleation sites facilitating the crystallization of the PET (T_c ≈ 190°C)\(^{10}\).

The glass fibers were observed to act as a nucleating agent for the crystallization of the neat polymers. This effect is more significant for the PET composite, which have a lower crystallization rate; the degree of crystallinity of the PET was increased from 15 to 26% with the incorporation of glass fibers whereas for the PA66 this increase was lower (34 to 38%). The overall crystallization of the blends in the PET/PA66/SGF composites follows the additive rule in relation to the PET/SGF and PA66/SGF.

### 3.3 Mechanical properties

The flexural modulus values for the PET/PA66 blends and PET/PA66/SGF composites are shown in Figure 6. The modulus values almost adhere to the additive rule with a slightly positive deviation, values ranging from 2.6 to 3.4 GPa for the blends and from 10.0 to 10.5 GPa for the composites. Since the modulus represents an almost elastic property, it is not dependent on the strength of the interfaces between polymer-polymer and polymer-fiber. Because the PET and PA66 have similar modulus values this property is not dependent on the polymer blend composition, but only on the glass fiber length, orientation and distribution in the polymer matrix.

The degree of reinforcement in the PET/PA66/SGF composites was evaluated through a comparative analysis between the experimental modulus values and the theoretical values obtained using the Halpin-Tsai model\(^{24}\). According to the Halpin-Tsai model, the modulus for a fiber-reinforced polymer composite can be expressed in terms of the corresponding properties of the polymer matrix and the fiber phase together with their proportion and the fiber geometry, using Equations 5 and 6:

\[
E_r = \frac{E_f}{E_m} = \frac{1 + \xi \cdot \eta \cdot \phi_f}{1 - \eta \cdot \phi_f} \tag{5}
\]

\[
\eta = \frac{(E_f/E_m - 1)}{(E_f/E_m + \xi)} \tag{6}
\]

In Equations 5 and 6, \(E_r\), is the relative modulus, \(E_f\) and \(E_m\) are, respectively, the moduli for the composite, matrix and fiber and \(\phi_f\) is the fiber volume fraction. The factor \(\xi\) is an empirical constant that describes the influence of the fiber geometry. For oriented short fibers with aspect ratios higher than the critical value (l/d)\(^{c}\) (Equation 4), the factor \(\xi\) equals 2.(l/d)\(^{c}\) for fibers oriented parallel to the stress/strain and it has a value of 2 for fibers oriented perpendicular to the stress/strain. Therefore, the modulus is at the maximum when the fibers are oriented parallel to tensile direction and minimum when the fibers are oriented perpendicularly.

The relative modulus values for the PET/PA66/SGF composites are shown in Figure 7 along with the values predicted using the Halpin-Tsai model (Equations 5 and 6). The matrix modulus values for composites were assumed to be those of the corresponding blends (Figure 6) and the modulus of the glass fiber was assumed to be 70 GPa. The relative modulus represents the improvement in this property for the composite in relation to the polymeric matrix. The experimental relative modulus values for the composites range between 3 and 4, which is very close to the maximum theoretical value for composites in which the fibers are oriented longitudinally in relation to the applied strain, indicating a high level of glass fiber orientation and reinforcement in the composites.

Figure 8 shows the tensile stress-strain curves for PET/PA66 blends (Figure 8a) and PET/PA66/SGF composites (Figure 8a).

The tensile strength values for the PET/PA66 blends and PET/PA66/SGF composites are shown in Figure 9. The PET/PA66 blends show a negative deviation from the additive rule. Since the tensile strength involves plastic deformation of the polymeric matrix it becomes dependent on the phase morphology and thus the blend composition. The tensile strength value for the PA66-rich blend (PET/PA66 25/75) was found to be between those for the neat polymers, while...
for the PET-rich blend (PET/PA66 75/25) and the blend with symmetric composition (PET/PA66 50/50) the tensile strength values were lower than those of the neat polymers. In contrast, the tensile strength values for the PET/PA66/SGF composites almost follow the additive rule with a slightly negative deviation, with values ranging from 129 to 155 MPa. These values are around twice those for the neat polymers, indicating, once again, the effective reinforcement of the polymer matrices with the addition of glass fibers. The glass fibers, with lengths exceeding the dimensions of the PET and PA66 phases, act as bridges binding the PET and PA66 phases and preventing premature failure in the interfacial region of the blends when the composites are overloaded.

The notched Izod impact strength values for the PET/PA66 blends and PET/PA66/SGF composites are shown in Figure 10. In general, the composites showed higher impact strength values (68-85 J m$^{-1}$) than the blends (26-42 J m$^{-1}$). This is a consequence of energy dissipation mechanisms, such as fiber debonding, pullout, bridging and fracture, which induce plastic deformation of polymeric matrix before failure. Bridging and fiber fracture are likely to occur as a consequence of the presence of a population of fibers which are longer than the critical length for effective reinforcement, while debonding and fiber pullout occur due to the presence of fibers which are shorter than this critical length value. The impact strength values for the PA66-rich blend (PET/PA66 25/75) and the respective composite (PET/PA66 25/75 30 wt% SGF) follow the additive rule. On the other hand, for the PET-rich blend (PET/PA66 75/25) and the blend with symmetric composition (PET/PA66 50/50) the impact strength values were similar to that for the neat PET (26 J m$^{-1}$), which, in turn, is lower than the value for the neat PA66 (46 J m$^{-1}$). Similar behavior was observed for the respective PET/PA66/SGF composites.

It is worth mentioning that the values for the mechanical properties of the PET/PA66/SGF composites are consistent with values reported in the literature for short glass fiber
reinforced composites based on post-consumer PET\textsuperscript{13,14} and PA66\textsuperscript{13,14}.

The mechanical properties of the PET/PA66/SGF composites reported herein (Figures 6 to 10) attest to the effective reinforcement of the PET/PA66 matrices through the incorporation of glass fibers, which is in agreement with the good dispersion of the blends (Figure 4), the homogeneous distribution, high level of orientation (Figure 3) and optimized dispersion (Figure 2) of the glass fibers within the polymeric matrices.

4. Conclusions

Composites comprised of bottle-grade post-consumer polyethylene terephthalate and virgin polyamide 66 (PET/PA66) blends and corresponding short glass fiber reinforced composites (PET/PA66/SGF) were investigated. In general, they showed good mechanical performance in flexural, tensile and impact tests. A high level of reinforcement was achieved in the composites, which was confirmed by comparison of the experimental modulus values with theoretical ones obtained using the Halpin-Tsai equation. The tensile strength and notched impact strength of the composites based on polymeric matrices with a PET content of 50\% or higher showed a negative deviation from the additive rule, whereas these properties were consistent with the additive rule for the composite with a PA66-rich blend matrix. There was evidence that PA66 and SGFs act as nucleating agents for PET, reducing the limitations associated with the use of post-consumer PET in engineering applications. In summary, the use of PET/PA66/SGF composites is an interesting strategy for obtaining new thermoplastic composites with good mechanical performance. In addition, this represents a promising alternative for the application of post-consumer PET, an abundant and cheap material, in the well-established market of PA66/SGF composites, which are widely used in technical parts with engineering properties.

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