EFFECTS OF PROCESSING ON CRYSTALLIZATION AND MECHANICAL PROPERTIES OF RECYCLED POLY(ETHYLENE TEREPTHALATE)/SHORT-GLASS-FIBER COMPOSITES

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Composites of recycled poly (ethylene terephthalate) and short-glass-fiber (PET/GF) with varying compositions (0-40 wt % of GF) were compounded individually in single-screw extruder (SSE) and co-rotating twin-screw extruder (TSE). The SSE was fitted with barrier flighted screw and TSE with a typical setup for this purpose was used. The composites were subsequently injection molding at two different mold temperatures (10°C and 120°C). The effects on crystallization, microstructure and mechanical properties of PET/GF samples were evaluated. Microstructure investigations show appropriate dispersive and distributive mixing of GF within the PET matrix regardless the composites are prepared in SSE or TSE. Accordingly, fine mechanical properties were achieved for all the composites. The good performance of SSE was attributed to the double flighted screw melting zone which allows fast and homogeneous melting of PET improving the mixing level of GF into the PET matrix. The mold temperature is an important processing parameter that influenced the mechanical properties of PET/GF composites by means of the control of the degree of crystallinity of PET.

Introduction

Short glass-fiber reinforced poly (ethylene terephthalate) composites (PET/GF) have been widely used to manufacture injection-molded articles for domestic, electrical and automotive applications where engineering properties such as high modulus, high toughness and thermal resistance are demanded (1⁻⁴).

In the work reported here, we studied the effects of extruder type (single- vs. twin-screw) and mold temperature (10°C and 120°C) on crystallization, microstructure and mechanical properties of injection-molded PET/GF samples with varying glass-fiber content (0-40 wt % in the composites).

Experimental

Materials

A waste bottle-grade PET in flake form with intrinsic viscosity of 0.70 dL g⁻¹ was used. The short-glass-fiber, provided by Vetrotex Saint-Gobain Company under code EC 983, is E-glass roving of 4.5 mm chopped filaments with fiber diameter of 10 µm and with an aminosilane sizing.

Methods

PET/GF composites containing different amounts of glass fiber (0, 20, 30 and 40 wt %) were prepared using two different extruders: a single-screw and a twin-screw extruder. The single-screw extruder (L/D = 32 and D= 35 mm) is fitted with a barrier double flighted screw in the melting section. It was operated at barrel temperature of 275°C and screw speed of 50 rpm. The materials were formulated by introducing all the components simultaneously into the hopper of the extruder during a single processing step. The twin-screw extruder, a Werner & Pfleiderer modular intermeshing co-rotating with L/D = 40 and D = 30mm, was set with a screw configuration comprising two staggered kneading blocks (45°) separated by a conventional conveying section. The barrel temperature profile was set at 275°C and the screws speed at 200 rpm. The PET was feed in the hopper by a gravimetric feeder. Glass-fiber was introduced into the molten PET by a side feeder in a location just before the second set of kneading blocks. The feed rate was set from 10 to 15 kg h⁻¹ in order to maintain the torque level constant at 85%.

Specimens for mechanical tests were injection-molded from the extrudates using HIMACO LH 150-80 machine at two different mold temperatures: 10°C and 120°C. The other operative molding parameters were kept constant: barrel temperature of 280°C, holding pressure of 650 bar and mold cooling time of 45 seconds.

The Polymer Processing Society 23rd Annual Meeting
Flexural tests were carried out according to ASTM D 790 in EMIC DL 2000 equipment at crosshead speed of 2 mm min\(^{-1}\). The Izod impact strengths were measured with CEAST Resil 25 pendulum using notched specimens according to ASTM D 256. The samples were conditioned at 23°C and 50% relative humidity for 48 hours prior to tests. Each mechanical test value was calculated as the average of at least five independent measurements. The standard deviations of each value were also calculated and are shown as error bars in the plots.

DSC analyses were performed to determine the degree of crystallinity of PET in the injection-molded samples. Scans from 20°C to 280°C at heating rate of 10°C min\(^{-1}\) and under N\(_2\) atmosphere (50 mL min\(^{-1}\)) were carried out in Shimadzu DSC-50 calorimeter. Samples (ca. 10 mg) were taken from injection-molded Izod bars. The degree of crystallinity of PET (X\(_c\)) was calculated using the equation: 
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X_c = \frac{\Delta H_c - \Delta H_m}{\Delta H_f},
\]
where \(\Delta H_c\) is the cold crystallization enthalpy and \(\Delta H_m\) is the melting enthalpy, calculated from the DSC thermograms, and \(\Delta H_f\) is the heat of fusion of 100% crystalline PET (120 J g\(^{-1}\))\(^{(5)}\).

The average length (L\(_a\)) of the fibers was determined by an Optical Microscope and an image analyzer on about 400 fibers. The fibers were recovered from the injection-molded impact bars by burning off the PET at 600°C for 3 hours.

The microstructures of the PET/GF composites were investigated using Philips XL 30 Scanning Electron Microscope (SEM). Samples were cryo-fractured from Izod bars and coated with gold using a sputter coater before observation.

**Results and Discussion**

SEM investigations, as illustrated for PET/GF 80/20 samples compounded in SSE (Figure 1a) and in TSE (Figure 1b), revealed good dispersive and distributive mixing of GF into PET regardless the composites are prepared in SSE or TSE. There are no bundles and the glass-fibers are uniformly dispersed throughout the PET matrix.

![Figure 1](image_url) – SEM micrograph of cryo-fractured surfaces of PET/GF 80/20 composites injection-molded with mold temperature of 120°C. Samples compounded in SSE (a) and in TSE (b)

Number average fiber length (L\(_a\)) values for injection-molded PET/GF samples were in the range of 220-340 \(\mu\)m, giving final fiber aspect ratios between 22 and 34, which are one-half to twice the critical value for PET. This ensures effective stress transfer from the PET matrix to the fibers as the composites are mechanically loaded.

The observations above show that the single-screw extruder that was used was able to generate suitable level of mixing for preparation of PET/GF composites as a co-rotating twin-screw extruder. The barrier double flighted screw zone provides fast and homogeneous polymer plasticization since it separates the melt pool from the solid bed in the screw channels\(^{(6,7)}\). For the PET/GF composites, it induces uniform dispersing of GF throughout the PET matrix and good distributive mixing of GF into the PET matrix because GF keep on with melted PET for a long time. Another important issue is that barrier screws are suitable for oxygen reduction in the molten polymer\(^{(8)}\), which is a factor that contributes to prevent PET degradation.

Figures 2 and 3 show, respectively, flexural modulus and Izod impact strength as a function of GF content for PET/GF samples compounded at two different extruder configuration (single- and twin-screw) and injection-molded using two different mold temperatures (10°C and 120°C).

For all PET/GF composites under study, the flexural modulus (Fig. 2) was found to increase monotonically with addition of GF, as a result of glass-fiber reinforcement. Besides, for each composition, no significant differences in the reinforcement level were observed in relation to the type of extruder (single- vs. twin-screw) where they were compounded. On the other hand, the mold temperature was found to influence this property. One can see a small
increase on the stiffness of the composites that were injection-molded at higher mold temperature (120°C), as compared to the ones molded at 10°C.

![Graph of Flexural Modulus vs GF Content](image1)

**Figure 2** – Flexural modulus of PET/GF composites

The Izod impact strength (Fig. 3) of PET/GF samples was also found to increase with addition of GF. However, as opposed to the modulus, the composites molded at lower mold temperature (10°C) presented higher values of impact strength. Moreover, practically no differences in impact strength were noticed for the composites in relation to the type of extruder where the composites were compounded, as observed for the flexural modulus values.

![Graph of Izod Impact Strength vs GF Content](image2)

**Figure 3** – Notched Izod impact strength of PET/GF composites

The mold temperature has significantly influenced the degrees of crystallinity of PET in the PET/GF composites (Figure 4). The compounding parameter (single- vs. twin-screw), however, was not observed to influence this property. Superior mold temperature (120°C) was found to lead to higher values of degree of crystallinity of PET. Higher mold temperatures reduce the cooling rate during injection molding and allows the PET chains to stay longer at about 165-175°C (interval of temperature where the rate of crystallization of PET exhibits a maximum), facilitating the spherulitic crystallization of PET. Also, a small increase in the degree of crystallinity of PET/GF composites were observed for samples with increasing amounts of GF, which suggests that GF acts as a nucleating agent for PET, in addition to the role as reinforcement.
Therefore, since PET/GF microstructures were practically unaltered with respect to the processing variables under study, one can assert that the degree of crystallinity of PET in the composites, controlled by the mold temperature in the injection-molding process, is the major responsible for the changes in the mechanical properties that were observed for each composition of the PET/GF under study.

Conclusion

The studies performed here on the PET/GF composites shown that a single-screw extruder with an appropriate screw design can replace successfully a typical twin-screw extruder to compound PET/GF composites with improved glass-fiber disperse and distribution within the PET matrix and enhanced mechanical properties. Barrier screw was attributed to be the key factor that determines the performance of single screw extruder for this purpose. In injection molding, the mold temperature was observed to be an important parameter that influences the mechanical properties of PET/GF composites by the control of the degree of crystallinity of PET in the PET/GF composites.

Acknowledgements

The authors wish to thank to FAPERGS for grant awarded to N. M. L. Mondadori.

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